

23C.  
2H  
2  
41  
43F  
0.2

FIELD MUSEUM OF NATURAL HISTORY

FOUNDED BY MARSHALL FIELD, 1893

MUSEUM TECHNIQUE SERIES

No. 3

---

RESTORATION OF ANCIENT BRONZES  
AND  
CURE OF MALIGNANT PATINA

BY

HENRY W. NICHOLS

ASSOCIATE CURATOR OF GEOLOGY

FORWARDED BY

BERTHOLD LAUFER

CURATOR, DEPARTMENT OF ANTHROPOLOGY

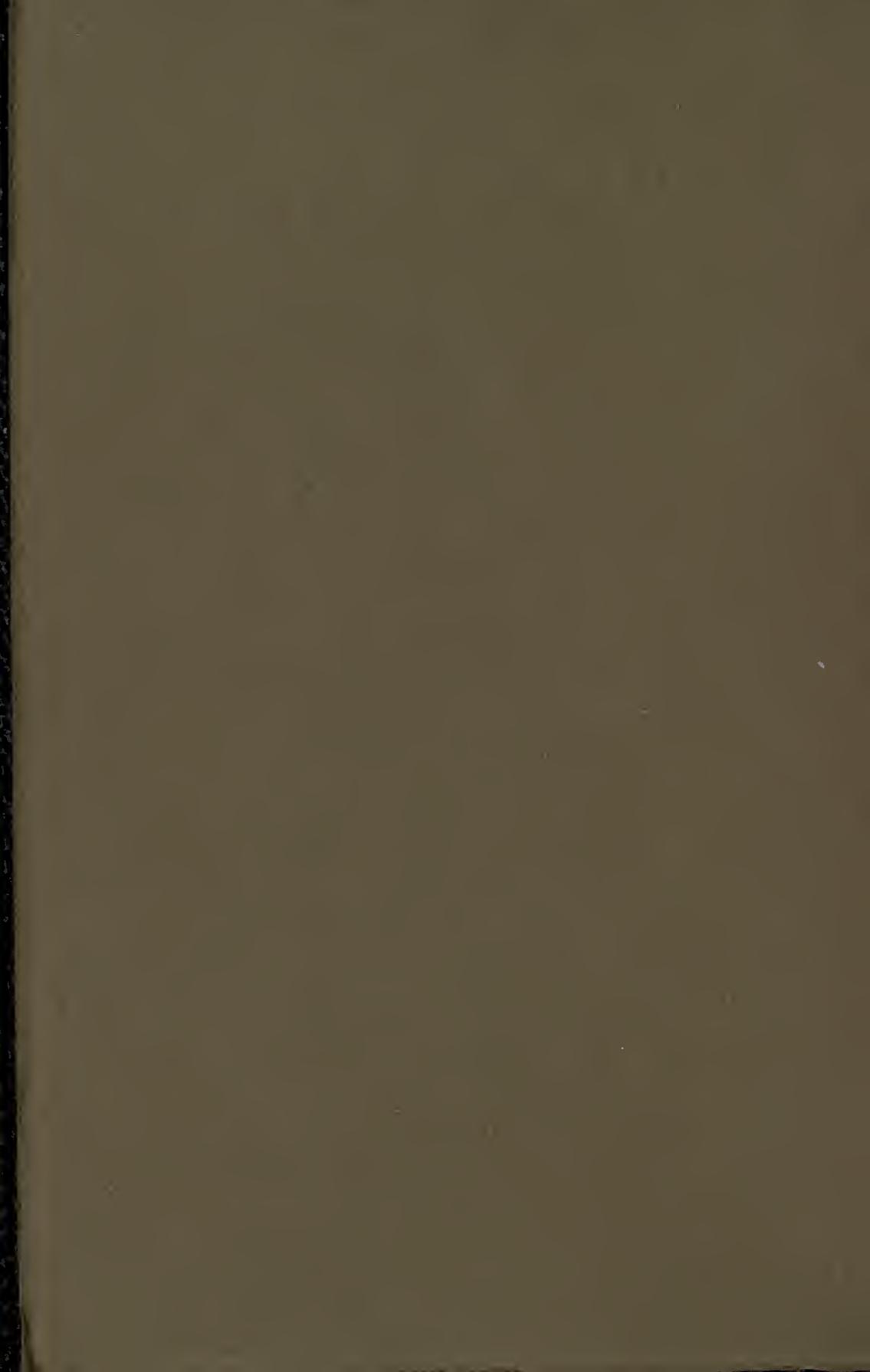
OLIVER C. FARRINGTON

DIRECTOR, DEPARTMENT OF ANTHROPOLOGY



CHICAGO, U. S. A.

AUGUST 9, 1930







BRONZE STATUETTE OF THE EGYPTIAN GODDESS, SEKHMET

Before and after treatment

Serious corrosion due to malignant patina threatened to destroy this priceless specimen. Treatment not only eliminated the malignant matter but exposed much delicate detail. Museum No. 31642.

FIELD MUSEUM OF NATURAL HISTORY

FOUNDED BY MARSHALL FIELD, 1893

MUSEUM TECHNIQUE SERIES

No. 3

---

RESTORATION OF ANCIENT BRONZES  
AND  
CURE OF MALIGNANT PATINA

BY

HENRY W. NICHOLS

ASSOCIATE CURATOR OF GEOLOGY

FOREWORD BY

BERTHOLD LAUFER

CURATOR, DEPARTMENT OF ANTHROPOLOGY

OLIVER C. FARRINGTON

CURATOR, DEPARTMENT OF GEOLOGY

EDITOR



77044

CHICAGO, U. S. A.

AUGUST 9, 1930

PRINTED IN THE UNITED STATES OF AMERICA  
BY FIELD MUSEUM PRESS

## CONTENTS

	PAGE
Foreword.....	5
Restoration of Ancient Bronzes and Cure of Malignant Patina ..	7
Apparatus Used at Field Museum .....	12
Treatment .....	19
Cleaning Treated Specimens and Preparing Them for Exhibition.....	35
Malignant Patina.....	45
Index.....	51



## FOREWORD

One of the modern developments of science is the close alliance of chemistry and archaeology for definite practical purposes. The archaeologist cannot dispense with the cooperation of a chemist who enables him to preserve and to restore the material discovered in the soil and entrusted to his care. In Mr. H. W. Nichols, Associate Curator of Geology, Field Museum has a veteran geologist and chemist who combines his technical knowledge and wide experience with an intelligent and sympathetic understanding of archaeological problems, as amply demonstrated by his Report on a Technical Investigation of Ancient Chinese Pottery, inserted in my monograph, *The Beginnings of Porcelain in China*. Another important contribution made by him to Chinese archaeology—a chemical analysis of one hundred archaic bronzes—still awaits publication.

The condition in which many Egyptian bronzes were found after years of exhibition in Field Museum and in which bronze vessels and implements excavated at Kish arrived here made it desirable to subject them to the Fink electrochemical process which has so successfully been inaugurated by the Metropolitan Museum of Art, New York. Associate Curator Nichols was placed in charge of this work. Familiarity with the process was acquired by treating a number of smaller bronzes to remove disfiguring crustations. In 1925 a beginning was made with two large and several small bronze figures from the Egyptian collection which exhibited bad cases of malignant patina. By that time the electrochemical process, carefully studied by Mr. Nichols, had been perfected to a high degree, and the treatment of the large bronze figures proved to be entirely successful. Not only was the fatal progressive corrosion checked permanently, but also unsuspected designs with much elaborate detail were revealed. During the four years 1926-29 a total of 360 bronzes, chiefly from Egypt and Mesopotamia, were restored to health by means of the electrochemical process.

The plates accompanying this treatise will teach sufficiently what the results of this process are. Bronze implements which were received here as shapeless and sometimes unrecognizable masses have now been restored to their original forms, and can be classified properly and studied. In many others interesting designs or inlays have been laid bare after the removal of the malignant patina. In each and

every case the objects thus treated have obtained a new lease on their lives and are permanently preserved. The advantages accruing to archaeology from this method cannot be overvalued and must be acknowledged with a deep sense of gratitude.

It is hoped that the detailed description of the technique given by Mr. Nichols on the following pages will benefit other institutions which are obliged to cope with the problems of restoring and preserving ancient bronzes.

BERTHOLD LAUFER

## RESTORATION OF ANCIENT BRONZES AND CURE OF MALIGNANT PATINA

---

BY HENRY W. NICHOLS

---

The Fink electrochemical process for the restoration of ancient bronzes has been in regular use at Field Museum for more than five years. This process, which was first developed by Professor Colin G. Fink at Columbia University for the use of the Metropolitan Museum of Art, has, in the laboratories of Field Museum, proved safe, simple, and easily applied. The remarkable results reported by the Metropolitan Museum<sup>1</sup> have been duplicated in every respect in Field Museum laboratories.

The Fink process reverses corrosion by electrolytic methods. It reduces the oxidized copper minerals of the incrustation to metallic copper. This copper forms as an incoherent slime which can be readily brushed away to expose the original surface of the bronze. The apparatus used is much like that employed in electroplating. The object to be treated is suspended as cathode between insoluble anodes in an electrolyte of dilute caustic soda. A weak direct current is passed through the cell until the crust disintegrates. The object is then taken from the electrolyte, the disintegrated crust removed, and the specimen prepared for exhibition by usual methods. The general method has been described in a publication of the Metropolitan Museum already referred to. The directions given by Professor Fink should be strictly adhered to, and even minor changes should not be made except for definite reasons accompanied by accurate knowledge of the effect of the change. Changes in strength of current or electrolyte may easily distort the bronze<sup>2</sup> or cause it to fall to pieces, or the copper may deposit as a coherent mass of metal difficult or impossible to remove.

Using the equipment and procedure described in detail on the following pages, Field Museum has found these troubles easily

---

<sup>1</sup>Colin G. Fink and Charles H. Eldredge, *Restoration of Ancient Bronzes and Other Alloys*, Metropolitan Museum of Art, 1925.

<sup>2</sup>The word "bronze" is used in this paper in its general sense to include both true bronzes, other copper alloys and copper.

## 8 FIELD MUSEUM OF NATURAL HISTORY—TECHNIQUE, No. 3

avoided and has had nearly uniform success. The bronzes treated are irreplaceable, and the process has, in consequence, been conducted with many safeguards, some of which may be unnecessary. These safeguards do not involve a material increase in the amount of labor required and seem to be amply justified by the results attained.

Much of the material treated in Field Museum has been in such a state that mechanical or chemical cleaning was hopeless, yet, even with these, failures are so few as to be negligible. Even specimens so altered that they appear to be mere shapeless masses of concretionary oxides will ordinarily resume their original forms, even to the restoration of incised decorations. Certain thin bronzes which appear to be wholly converted to silicate of copper have thus far failed to respond to treatment, but they have not been injured by the attempts to treat them.

The process has two disadvantages. It requires special equipment and close supervision by a man skilled in handling antique bronzes and by a skilled chemist. Most art and archaeological museums have experts on their staffs who can handle the bronzes properly, but the chemical skill necessary to carry out the electrolytic process safely and effectively will in many instances be lacking. This Museum, however, has been able to train an assistant accustomed to handling bronzes but without chemical knowledge so that he can treat all ordinary specimens with but general supervision by the chemist. The latter, accordingly, has to give close attention only to the more difficult objects. It should be possible, therefore, for museums where chemical skill is not available to treat with fair success bronzes that are not in too bad condition if sufficiently detailed information is available. This account of procedure at Field Museum is intended to supply such information. When the process is employed without competent supervision, results such as those secured at the Metropolitan and Field Museums should not be expected; yet it should be possible to save many specimens that could not be treated in any other way, and to secure superior results with specimens that would ordinarily be treated by older methods.

Success will depend upon following instructions rigidly. When ten grams of a substance are called for, it means ten grams carefully weighed out. Anyone who, after weighing out a few lots, attempts to estimate the quantity thereafter, will ruin his specimens. Likewise, one liter means a quantity of liquid reaching exactly to the

liter mark on the graduate. Attempts to estimate the quantity by eye will not do. One and six-tenths amperes of current means that a reliable ammeter must read 1.6 during the whole time that the electrolytic cell is in operation. Also, all chemicals must be of the quality specified and must be kept in good condition. Most failures will be due to carelessness in these respects. While some variations from the rigid conditions prescribed are necessary for the best results, they should not be attempted without advice from a chemist unless after long experience.

Many ancient bronzes are well preserved and call for no treatment beyond simple cleansing. Others, which have been long buried in contaminated soil or long subject to the action of impure or mineralized waters, are seriously corroded, and much of their value has been lost. These require treatment to restore, as far as possible, the original form. In many of them corrosive action continues so that even under museum conditions their complete destruction is only a matter of time. For such as these, treatment is imperative. Restoration is easy or difficult according to the stage to which decomposition has advanced. The causes and nature of the corrosion and detailed descriptions of the structure and composition of the coatings and alteration products have been adequately discussed by Dr. Frederick Rathgen<sup>1</sup> and by Professor Colin G. Fink and Mr. Charles H. Eldredge.<sup>2</sup> Only sufficient discussion of the nature of the corrosion and of the corroded products is provided here to permit an intelligent application of the process.

Many bronzes are merely covered with a thin, semi-transparent coat of copper minerals of pleasing color, which does not materially obscure detail. This is a patina which, if it is not of a destructive nature, should be carefully preserved. The metal surface under such a patina is usually smooth and in good condition. When it is roughened or pitted, the surface under a patina of this description cannot be improved by the methods described.

When the coat becomes thicker, it loses its translucency, tends to become rough, and often seriously obscures detail. Often the beauty of the thickened patina and the appearance of antiquity given by it justify its retention. In many cases, however, important detail is obliterated, and removal of the coat is desirable. Although the metal surface under the coating is often perfect, on some specimens it is

---

<sup>1</sup>Die Konservirung von Altertumsfunden (Berlin, 1898); The Preservation of Antiquities, 1905. English translation, University Press, Cambridge.

<sup>2</sup>Op. cit.

roughened or even deeply pitted. In such cases the Fink treatment may be so conducted that the surface will be much improved or even restored to practically its original smoothness. In the case of many bronzes, particularly the more ancient, the metal of the original surface has completely gone, and only a shapeless metal core remains. It has been found that the oxide of copper which replaces the original metal surface retains the detail of that surface, so that by appropriate treatment it can be restored even to its minute details. This is also true in cases where the last of the metal core has disappeared. Surfaces thus restored are often smooth. Many of the surfaces, however, are rough or pitted. Roughness of the coating is, in general, no indication of the state of the surface below. If, however, the surface is a botryoidal mass of malachite or azurite, the surface of the original specimen when restored will be badly corroded. When the exterior surface of the untreated mass is reasonably smooth (except for included sand grains), but shows a few lumps of botryoidal malachite or azurite, then there will be on the restored surface a badly corroded spot directly under the malachite lump. This is true even when the malachite lump is minute. Corrosion pits can frequently, not always, be caused to partially or completely fill with restored metal, thus partially or completely recovering the smoothness of the original surface. Of course, any engraved ornamentation of the original will be lacking on such spots. The restoration of such surfaces is much more difficult than the treatment of better preserved material and requires experience and great delicacy of handling. All surfaces to be restored from the oxidized state, whether pitted or not, are naturally fragile, and must be handled with great care until they have been hardened at the end of the treatment.

Although many of the heavily encrusted bronzes are outwardly deformed, the deformation is usually confined to the crust. Unless the bronze is thin, the restored specimen is seldom deformed. Occasionally a specimen is encountered which has swollen and become distorted as a consequence of oxidation of the metal of its interior. Ordinarily, however, a reasonably heavy bronze seems to resist the distorting forces as the excess material from oxidation migrates and is deposited in the crust. Many thin specimens, such as bowls, mirrors, and similar objects, are warped. Some of the bending is due to accidental pressure from outside, but much of it is a consequence of corrosion. Long, slender objects like needles and pins are usually bent, even when otherwise in good condition. Electrolytic treatment

cannot correct this kind of distortion. There is another kind of deformation often found which can be corrected. The bronze may be fractured and the fracture healed by deposition of copper minerals. The crystallization of these minerals has exerted sufficient pressure to push apart the pieces of bronze, thus enlarging the specimen. Often these layers of mineral are wedge-shaped and the form of the bronze is changed. During electrolytic treatment these cementing minerals are disintegrated and the bronze separates into its individual fragments. These may be recemented, and the bronze restored to its undistorted size and shape. There may be only one such cemented break or there may be many.

Many bronzes which have passed through the hands of dealers have been restored by modeling over the surface with some plastic. The amount of restoration varies from a simple smoothing of a pitted surface to the building of a complete new figure over a core of badly corroded bronze. It is often desirable to remove this added material, and nothing of the kind has yet been encountered in this laboratory that does not yield to electrolysis. Many Egyptian bronzes have been restored with a plastic that appears to be a mixture of brass or copper turnings, sal ammoniac, and wax. This mixture contains corrosive material which may become active at any time. It yields readily to the Fink treatment. It is usually convenient to remove most of it by a preliminary submergence in hot water to melt the wax.

The Fink treatment also removes artificial patina, whether of chemical origin or applied as paint. Artificial patinas and restorations must be removed when they cover a malignant patina which is or may become active.

The most serious problem encountered by those entrusted with the preparation and care of antique bronzes has always been treatment of malignant patina. This is a coating of so corrosive a nature that if unchecked the smallest patch will in time destroy the entire bronze. It is erratic in its action; a patch of it may remain passive for years and then for no apparent reason suddenly become active. Removal of every trace of this substance is imperative. The common and probably the only form of malignant patina is an oxychloride of copper, a substance which has the property of transferring oxygen from the air to copper or copper alloys, thus corroding them without itself being destroyed in the process. A small quantity of the oxychloride can corrode an indefinitely large quantity of copper or bronze. This oxychloride is pale green in color and often more or less powdery in texture. It may be recognized after some experience,

## 12 FIELD MUSEUM OF NATURAL HISTORY—TECHNIQUE, No. 3

although its appearance is closely simulated by mixtures of carbonate of copper with oxide of tin which are of common occurrence. The coat of malignant patina is commonly patchy. Often only a single, minute fleck is present. Frequently the bronze surface is thickly covered with these small flecks. Often there are patches of malignant patina of considerable area in one place while the rest of the surface is free from it. Heavily crusted bronzes, especially such as have lost much of the form of the underlying bronze, are frequently more or less unstable, owing to the dissemination of oxychloride through their substance. Such specimens should be kept as dry as possible until they are treated.

Malignant patina is a consequence of earlier, often slight, corrosion by salt in the presence of moisture. This happens when specimens have long been buried in contaminated soil or impure water. The salt in such soils and waters sometimes comes from sea or mineral water but generally arises from contamination by organic wastes. The oxychlorides thus formed adhere to the surface and are occluded in the pores. They continue destructive action indefinitely even after the bronze has been removed from the primary source of trouble.

There are two ways by which bronzes may be infected by malignant patina during their preparation and restoration: (1) Repairs may be made with cements and plastics which contain chlorides. Bronzes of Egyptian origin secured from dealers are often repaired with such material. Occasionally there is active corrosion under the added plastic which in such cases must be removed or the specimen will be lost. (2) Another source of infection is the use of hydrochloric acid for dissolving the crust. This acid should never be used for the purpose. Some specimens may be successfully cleaned with acid but only dilute nitric acid should be employed if a mineral acid is used at all. After treatment with acid the specimen should be momentarily immersed in limewater. In many afflicted bronzes the destructive agent remains for a long time and possibly permanently passive, but such objects must be watched. Treatments for malignant patina are discussed in a later section.

### APPARATUS USED AT FIELD MUSEUM

Experienced electrochemists and electrical engineers will not need the detailed description which follows. Such men are competent to design their own equipment. When, however, the apparatus must be assembled by those less experienced, the following detailed

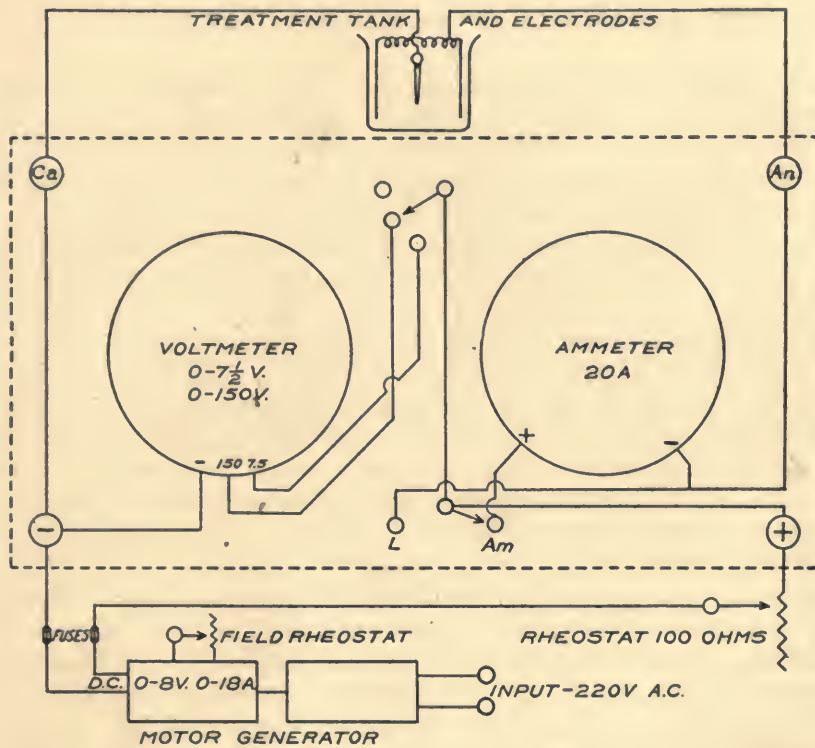


FIG. 1  
Schematic diagram of electrochemical apparatus

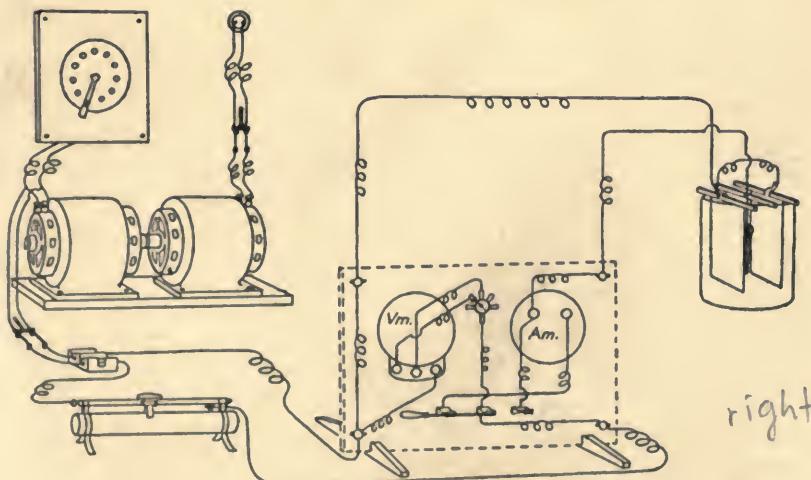


FIG. 2  
Picture diagram of electrochemical apparatus

## 14 FIELD MUSEUM OF NATURAL HISTORY—TECHNIQUE, No. 3

description of an equipment which has given satisfaction over a period of years should be helpful. Although the apparatus as described may seem complex, it is really very simple. If each part is considered separately its erection should not be difficult for one of mechanical bent who has elementary knowledge of electricity.

The apparatus is not unlike that used for electroplating on a small scale and in fact is used occasionally for that purpose. It comprises (Fig. 1), a source capable of generating low voltage current over long periods, means of measuring and controlling this current, electrolytic tanks, sheet iron for electrodes, chemicals and various accessories, such as graduates, scales and dishes. Means for checking strength of solutions and for chemical analysis are available and are occasionally used. The tools of the archaeological preparator, such as brushes, cleaning tools and lacquers, are used in the final stages of the treatment. Suitable tanks for washing in running water and in boiling water are needed. All electrical apparatus and connections are shown in the diagrams (Figs. 1 and 2). The ordinary equipment of the Museum laboratories provided most of the necessary apparatus and what had to be added has been so selected as to be useful for other purposes. As the apparatus is used for a variety of purposes it has been found convenient to install the equipment for the first or electrical part of the treatment in the chemical laboratory and to transfer the bronzes to an archaeological laboratory for finishing.

*Current supply.*—Current is provided by a small motor generator which also supplies current for electrolytic copper and nickel analyses. It is fed by a 220-volt power line. Its output is a direct current which may be regulated to any value up to eight volts or twenty amperes, provided its maximum capacity of forty-five watts is not exceeded. It is regulated by a rheostat in the field winding of the generator. Its capacity has thus far been ample for all purposes. The voltage required seldom exceeds three and one-half volts, except for the preliminary breaking of an insulating coat which is sometimes present. Current requirements for most treatments are below four amperes, although the full twenty-ampere maximum of the machine has been used for some large bronzes. This machine runs all day without attention and maintains its output constant, so that no time need be wasted watching meters. A motor generator for this process should have the following features:

Maximum output, 50 to 100 watts; maximum voltage, 8 to 12; maximum current, 18 to 25 amperes; control by rheostat in the field

winding should be by steps not greater than 1 to 2 amperes; output under constant load should not fluctuate; should be rated to run all day with maximum output.

If bronzes of more than 500 square inches of surface are to be treated, a larger machine is needed, but the small machine is more convenient for ordinary work. The high first cost of a motor generator is amply compensated by its ease of operation and freedom from trouble.

Other sources of current supply are possible and some one of these may be better adapted to conditions in some laboratories, but an attempt to use batteries or storage batteries is not recommended.

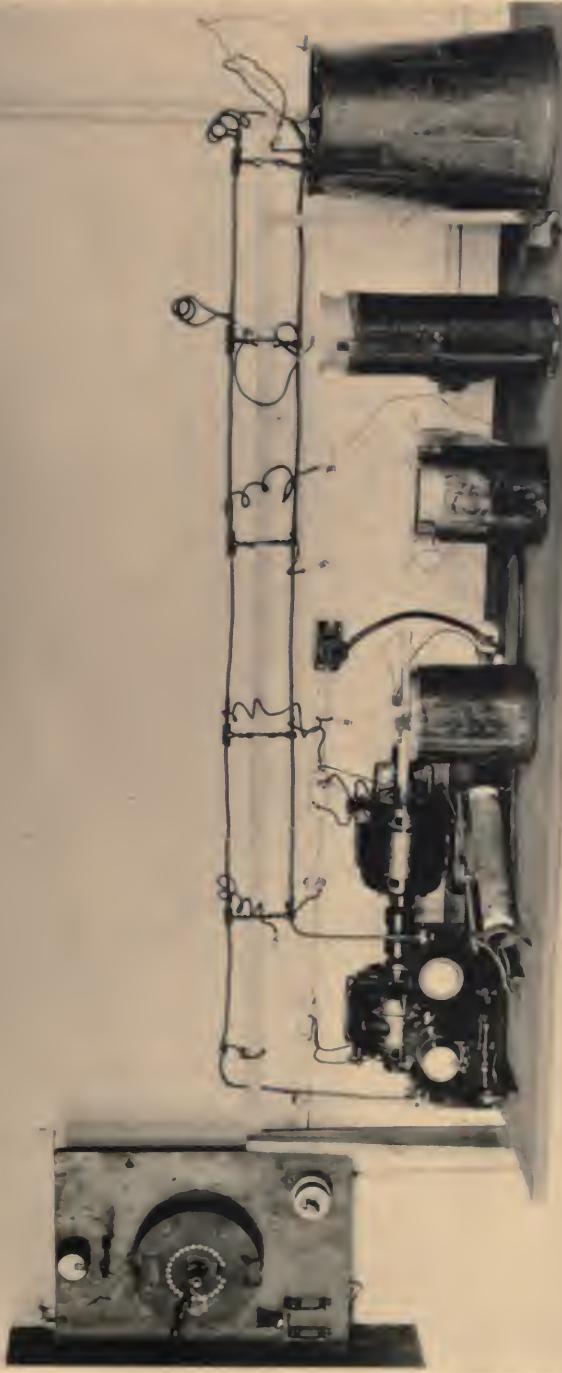
*Current control.*—To guard against damage from short circuits there are two fuses through which the two output wires from the motor generator pass. Fifteen-ampere fuses are used. These are replaced by the thirty-ampere size when ten or more amperes of current are employed. Currents ranging from a few tenths to twenty amperes are used and these must be maintained with a fair degree of accuracy. Currents of more than two amperes are regulated by the rheostat on the motor generator but for lesser values an external rheostat must be employed. This is a sliding contact instrument of the usual laboratory type. It has a maximum resistance of 100 ohms and a current rating of two amperes. It cannot be permitted to function when more than two amperes are used, as these heavier currents would destroy it. At such times the slider is left in the cut-out or short circuit position. This rheostat is placed between the motor generator and the measuring panel. Two wires carrying the output of the generator run to the measuring panel. One of these wires, it is immaterial which, is cut and the rheostat connected between the cut ends. Currents of less than two amperes are controlled by moving the slider.

*Measuring instruments.*—The effectiveness of the treatment and the safety of the specimens depend upon accurate knowledge and control of conditions at all times. Therefore, an accurate ammeter and voltmeter must be used. The instrument panel assembled at the Museum is simple, efficient and convenient. The instruments are mounted upon a seven- by fourteen-inch piece of bakelite three-sixteenths of an inch thick, supported by two wide, low, wooden feet. An ammeter, a voltmeter, two switches and four binding posts are mounted on this panel. The ammeter is a Weston type 301 instrument which reads to twenty amperes. The voltmeter is a Weston

## 16 FIELD MUSEUM OF NATURAL HISTORY—TECHNIQUE, No. 3

type 489. This is a double range instrument reading to seven and one-half and to 150 volts. Current enters the panel through two binding posts marked + and −. A wire connects the + post to the center terminal of a double throw switch. Another wire runs from an outer terminal of the switch to the + connection of the ammeter. The negative post of the ammeter connects by wire with another binding post marked *An* (anode). A wire from the anode post to the third terminal of the double throw switch completes the wiring for the ammeter. The switch throws the meter in and out of the circuit. As large currents of low voltage are occasionally used, the wires must be large or they will overheat or make trouble in other ways. The Museum panel is wired with 6-gauge bare copper wire. The double throw switch must have a rating of at least twenty amperes. Connections for the voltmeter are of ordinary bell wire, as this instrument draws only a minute current. These connections are made through a three-point switch by which the voltmeter may be cut out or its high or low range cut in at will. The switch is assembled from a switch post and points of the kind formerly used on radio sets. The center post is connected by bell wire to the anode binding post. Two of the switch points connect by bell wire to the high and low range posts of the voltmeter. The third point is left blank. It is important that the switch connections lie in the following order: blank, high, low. The negative post of the voltmeter is connected by bell wire to the cathode binding post. The input binding post marked − is connected by a short copper strip to a binding post marked *Ca* (cathode). Binding posts are marked with white oil paint and positive outlets and wire ends are marked with red paint. The wiring of the panel is shown on the diagrams (Figs. 1 and 2). Two 14-gauge wires run from the anode and cathode posts of the measuring panel along a rack from which connections to the electrolytic tanks are made. This rack is merely a wooden rod six feet long, supported eighteen inches above the bench. The wires are supported about an inch above and below the rod by ties of the same heavy wire. At intervals of a foot, short branch wires hang from these two mains. The electrolytic tanks connect with these short wires.

*Electrolytic tanks.*—Cylindrical battery jars are used for most small objects. A variety of bottles and earthenware crocks are also used at times. Large paint pails made of black iron are convenient for larger objects and occasionally it has been necessary to use a steel barrel. Any convenient receptacle made of glass or earthenware can be used. Black iron tanks with welded joints are good. Nothing



EQUIPMENT FOR ELECTROCHEMICAL TREATMENT OF BRONZES AND COPPERS IN FIELD MUSEUM

This occupies a shelf space of only 30 by 75 inches



## COPPER OBJECTS FROM KISH

Before and after treatment

1 and 2. Square-headed chisel, Field No. V-748. Length 4.8 in. Condition good. The copper wire which conducted current during treatment is wrapped around it, as is sometimes necessary. Treated at 0.2 ampere for two days. 3 and 4. Hair-pin without head. Field No. 405-L. Length 8.7 in. Condition fair. Treated at 0.25 ampere for two days.

that has been tinned, galvanized, soldered or brazed can be used. Attempts to use paraffined wood have not been successful because of leakage. When iron receptacles are used the receptacle can frequently be made the anode and separate anodes are not needed.

*Electrolyte.*—This is a 2 per cent solution of caustic soda. At first the chemically pure quality of caustic soda in distilled water was used, but it was soon found that chlorides from the bronzes so strongly contaminated the electrolyte that the quantity of chlorine in tap water and in the better grades of technically pure caustic soda was inconsequential. Accordingly, the technical grade of caustic soda in stick form is now used. The brand used shows but slight contamination with chlorine when tested by silver nitrate. The avidity with which caustic soda absorbs moisture and carbonic acid from the air makes necessary certain precautions when storing and handling it. It is advisable to purchase it in small containers. This laboratory receives it in one- and five-pound snap-top tins. Solutions are made immediately before use. After the weight of caustic needed is calculated, the empty tank is placed near the balance, the necessary weights are placed on the balance pan and then the top of the can of caustic is removed. The sticks of caustic are then placed on the balance pan (using crucible tongs for handling) and the weighing completed to the nearest gram with all possible expedition. The snap-top is then placed on the container as quickly as possible, after which the caustic is transferred from the balance to the tank by crucible tongs. The tank is then filled to the mark with water. In spite of the exercise of the greatest care it will often happen that the last of the caustic in a can will be noticeably wet. When this occurs it is well to reject the damp material. In deciding whether or not to reject damaged caustic it is well to remember that these bronzes are valuable and that the cost of a single bronze would buy much caustic soda.

In preparing the electrolyte the water is measured and the caustic weighed to the nearest gram. The water could as well be weighed, but in this laboratory measuring is more convenient. Ordinary laboratory graduates and coarse balances are used. The balance is a Gaertner of one kilo capacity, weighing to one centigram. Each tank is filled to a mark near the top, the water measured and the measure recorded, so that it is not necessary to remeasure for each treatment. As the weights and measures are metric, calculation of strength of solution is a simple matter, 2 per cent of the volume in cubic centimeters being a sufficiently close approximation to the

quantity of caustic soda in grams. As the technical grade of caustic is not absolutely pure, the solution is slightly under strength, but experience has shown that the deficiency is not enough to do harm. Solutions could be made from caustic, damp from exposure to the air, by diluting solutions to the proper specific gravity as determined by hydrometer or Westphal balance. The proper specific gravity is 1.0207 or 2.9° Beaume at 20° C. Such solutions would nearly always serve, but there is always the danger of excessive amount of carbonate in an occasional lot of damp caustic and on account of the value of the objects treated it is well to avoid this danger even if it is but slight. Also, as the solutions are made frequently and in small quantities, the value of the time consumed in the tedious adjustments of strength must be considered. These solutions should never be made until needed, as they absorb carbonic acid from the air and attack glass. It is also good practice to use fresh electrolyte for each lot treated.

*Anodes.*—Anodes are cut from stovepipe iron with tinners' snips. When an iron tank is used the tank itself is usually made the anode. Each anode has a lug about one-half inch wide and about two inches long, projecting from the top. Two small holes are drilled, not punched, in the lug and the end of a copper wire about a foot long is threaded through the holes and firmly clamped against the iron surfaces with pliers. Iron tanks used as anodes have a binding post permanently attached near the top. At first a number of specially shaped anodes were used but this practice has now been abandoned and two general forms are employed for nearly all purposes. Some shapes of bronze still require special anodes which are described later under the section treating of electrolytic treatment. Plate anodes are used for many specimens. These consist of two sheet-iron plates (Fig. 3) suspended on two sides of the bronze. These descend to within an inch from the floor of the cell and are as wide as the cell dimensions permit. They extend above the surface of the electrolyte and hang from a wooden rod lying across the top of the cell. The lug to which the wire is attached is bent to form the hook by which the anode is suspended. Another anode shape more used than the plate form is the liner anode, a sheet-iron lining which lies against the inner vertical wall of the cell (Fig. 4). This may seem an inefficient anode and it would be if current consumption were the important consideration, but it has been found that the farther the anode is from the cathode, the more regular is the action of the

current on the treated surface. Anodes can be used repeatedly until they are destroyed. Usually they last for dozens of treatments, but when bronzes badly contaminated with chlorides or sulphates are treated an anode may be destroyed by a single use.

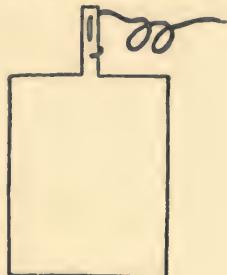


FIG. 3  
Plate anode

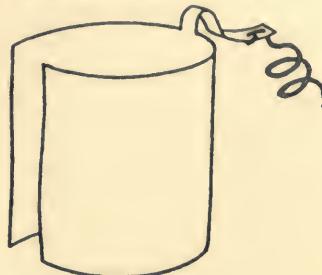


FIG. 4  
Liner anode

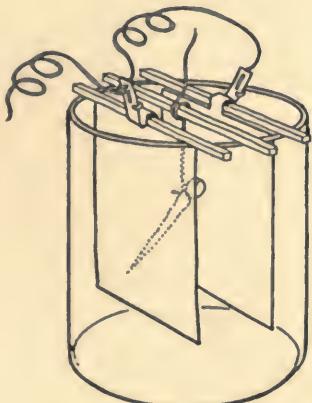


FIG. 5  
Electrolytic cell with plate electrodes

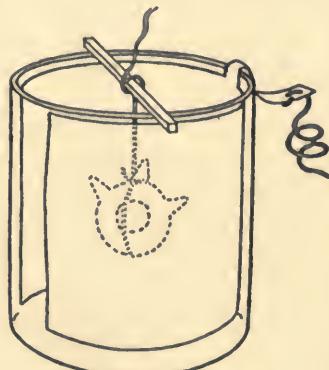


FIG. 6  
Electrolytic cell with liner electrode

Bare copper wire is used for connections and for wrapping friable specimens. The size most used is 26-gauge. Some 30-gauge is used for wrapping specimens that may fall apart under treatment and heavier wire is used when larger specimens are treated. This concludes the description of apparatus used for the electrical part of the treatment.

#### TREATMENT

The Fink electrolytic process is especially adapted to copper and bronze restoration. Doubtless it is effective for other alloys rich in copper but the writer has had no experience with such. Gold is readily treated by simpler means. Inlays of silver on bronze are not damaged when the silver is in good condition. All silver inlays on

bronze thus far encountered have been in good condition save for a thin, black tarnish. The bronze apparently protects the silver. Field Museum has had no experience with such silvers as are treated at the University of Pennsylvania Museum and such as are described by Fink and Eldredge.<sup>1</sup> The few small silvers received at the laboratory have been in bad condition. They appear to be wholly converted to chloride and are very porous. They have no crust and the surface is granular with none of the original detail remaining. They appear to be extreme examples of the decuperized silver described by Fink and Eldredge.<sup>2</sup> Attempts to treat these produced only a tangle of loose threads of silver. The treatment has no effect on iron.

A few bronze or copper bowls of the most ancient origin which have been encountered among the specimens submitted and which were formed from thin metal seem to have altered largely to silicate of copper. These resist electrolytic treatment, but are not damaged by it. They are perfectly stable and attractive in appearance so that there is no reason to treat them except to develop obscured ornamentation.

Among the more antique bronzes there are occasionally found specimens so completely changed that they cannot be restored. These are of rare occurrence, only three or four having thus far come to the Museum laboratories. Such objects are swollen to many times their original size. Their substance is a reddish-brown, weakly coherent powder covered with a skin of firmer material colored brown, green or sometimes blue. Usually long, deep, longitudinal cracks lined with malachite are present. These are specimens from which all metal has been removed and deposited as concretion outside the original boundaries of the object. The space originally occupied is either empty or filled with clay, sand or silt.

Unfortunately there is no way of recognizing such material in advance. Most bronzes of this external appearance can be restored successfully. The only practical procedure is to put all material of this character through the process. Afterwards those that do not yield to the treatment may be restored to the form and appearance they had when received. (Plate VII, Fig. 6.)

Lapis lazuli, turquoise, onyx and other mineral ornaments mounted on bronze or copper are not injured by the Fink process nor are ivory and bone. Fresh material of this nature would often be damaged by

---

<sup>1</sup>*Op. cit.*, p. 24.

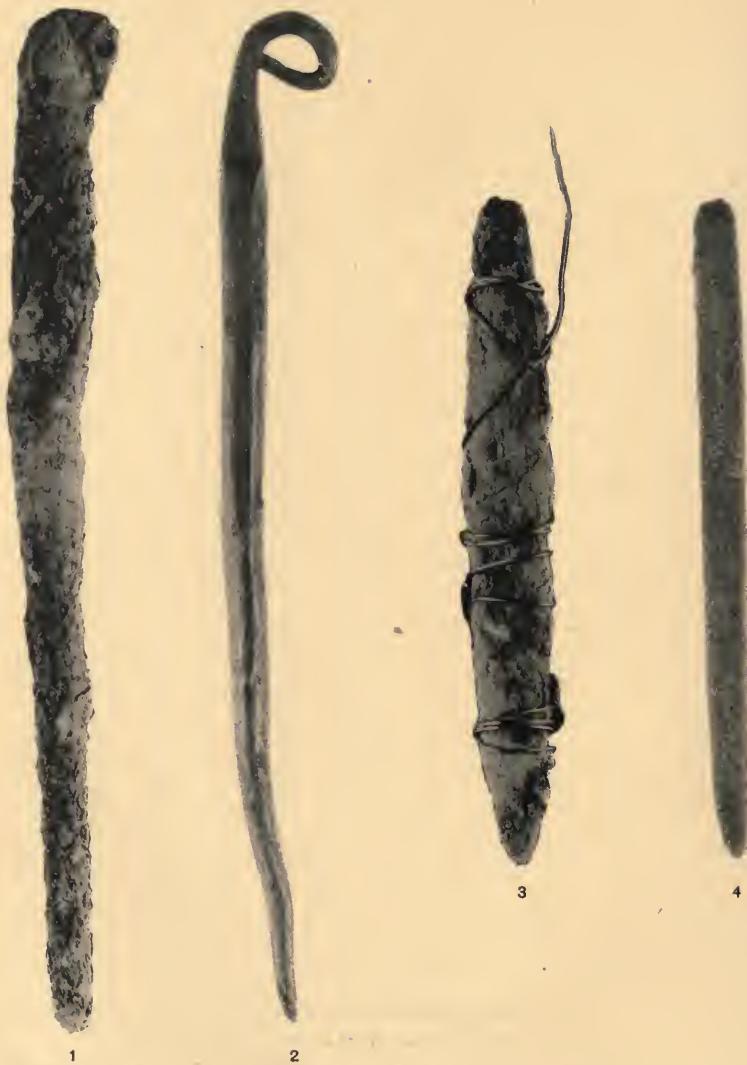
<sup>2</sup>*Ibid.*, p. 27.



## COPPER HAIR-PINS FROM KISH

Before and after treatment

1 and 2. Hair-pin, Field No. V-748. Length 4.7 in. Condition good. Treated at 0.25 ampere for two days. 3 and 4. Hair-pin with scrolled head. Length 4.5 in. Condition bad. Treated at 0.2 ampere for two and one-half days.



## COPPER OBJECTS FROM KISH

Before and after treatment

1 and 2. Hair-pin with scrolled head and blunt point. Length 4 in. Condition fair. Treated three days at 0.25 ampere. 3 and 4. Rectangular pointed tool with a coating of brown oxides and gray soil. Length 2.9 in. Condition poor. The wire which conducted current is shown wrapped around the specimen to increase electrical contact.

immersion in caustic electrolyte but in these ancient bronzes and coppers deterioration from age has proceeded so far that the caustic solution causes no additional injury. Nevertheless, it is well, whenever possible, to protect such material in the manner described on page 26.

Restorations and repairs are usually destroyed. Field repairs, where parts of broken objects have been cemented for temporary preservation, are readily noted and cared for. The cement disintegrates and the parts separate. This does no harm when the condition has been anticipated, as the parts are readily recemented later. Bronzes that have passed through the hands of dealers or that have received treatment in anthropological laboratories often have the joint so skillfully made that its presence is not suspected. The parting at such joints need not and usually does not injure the bronze, but does complicate and prolong treatment. Many bronzes have had pits on the surface filled in and missing parts restored with a variety of cements. Such bronzes sometimes need treatment to remove malignant patina. The material used for restoration usually disintegrates.

Much trouble is experienced with Egyptian bronzes purchased from dealers. Many of these are extensively restored with what appears to be a mixture of wax, brass turnings and some chloride, probably sal ammoniac. This restoration is sometimes so extensive that the restored figure has little resemblance to the original. When the restoration is well done and covered with a painted-on patina it is often impossible to detect restored areas. The chlorides in the material used for repairs induce in time an extensive, deep-seated and active malignant patina. Its treatment is therefore imperative. It is the practice in Field Museum to give such bronzes a preliminary treatment in boiling water. This melts the wax which rises to the surface of the water and the restoration disintegrates. This reduces the time of treatment. The artificial patina disappears and leaves the bronze bright.

Sometimes buried bronzes fracture from strains induced by ground movements or from contraction strains caused by removal of some of their substance by solution. The breaks often heal by deposition of mineral matter which forms a cement. When the cement happens to be a copper compound the treatment destroys the mineral and the joint opens, allowing part of the bronze to fall to the floor of the tank. This complicates the treatment, but does not permanently injure the specimen, as the pieces can be recemented

later. These naturally cemented fractures are often concealed under incrustations and when visible it is not always possible to recognize their nature. Sometimes such fractures remain open and the parts are held together only by the incrustation, so that an object apparently whole may be actually composed of a number of pieces. Such fractures can seldom be seen and cause some trouble.

The object of the treatment in most cases is to remove incrustations which conceal or disfigure the bronze and to restore to the object its original appearance. During treatment for this purpose corrosive substances which cause rapid disintegration are removed and the permanence of the specimen assured. It is employed also when a too thick patina obscures elaborate engraving of more value than the patina. An important use is for the elimination of malignant patina when it is so strongly developed that surgical or chemical means are ineffective. Bronzes are given the treatment without preliminary cleaning.

*Sorting.*—The bronzes are arranged in such order that, so far as is convenient, specimens of approximately the same size and condition may be treated together.

*Recording.*—The specimens are then entered in the laboratory record. The treatment destroys all identification numbers and tags attached to the specimens are often destroyed. When not destroyed they must be separated from the specimen at some stages of the treatment. The record must, therefore, contain data which will permit later identification. It also notes the character of the surface and the general condition of the object. Special attention is given to such features as "boils," warty protuberances which usually indicate serious pitting, fractures or repairs.

*Computation of surface.*—There is a maximum ratio of current to surface treated which must not be exceeded except in special cases. Attempts to estimate irregular surfaces by inspection frequently give figures far from the truth. Therefore, rough computations which give some approximation of the surface areas are made. Methods are used which underestimate rather than overestimate, so that the error does no harm beyond increasing the time of treatment. Calculations giving a close approximation to the true area are tedious in the case of complex forms and involve an unnecessary waste of time, whereas the rough calculations are rapidly performed. If the calculated area is materially in excess of the true, which need never

happen, conditions in the electrolytic bath will disclose the fault and it can be remedied before harm is done. It is probable that these calculations can be omitted and the current density regulated in conformity with appearances in the electrolytic bath. The computation takes very little time and is an additional safeguard. It also compels a second close examination of the specimen which sometimes discloses fractures or other features which require attention. For purposes of computation the bronze is considered as made up of a collection of simple geometrical figures. Minor irregularities are disregarded and no close coincidence of the geometrical and the actual figure is expected. The geometrical figures used for computation are the sphere and its parts, the cone and its frustum, the pyramid and its frustum, the cylinder, the prism and other simple forms with surfaces which can be readily computed. For the computation the tables and formulae in Hodgman's Handbook of Chemistry and Physics<sup>1</sup> are used.

The methods used are best shown by examples.

1. Pin without head. Length, 8.5 in., diameter of top, 0.4 in., tapers to point. This is a cone. The formula for the curved surface is  $\pi r \sqrt{r^2 + h^2}$ . The value of  $r^2$  is in this example small and may be disregarded, so the formula becomes  $\pi r h$ .  $r$  is half the diameter of the base or 0.2.  $3.14 \times 0.2 \times 8.5 = 5.3$  sq. in.

2. Ear ring. No. V 747-1. Diameter of ring 1.8 and 1.6 in. Diameter of wire, 0.22 in. Overlap of ends of wire, 0.6 in. It is near enough to consider this a circle of 1.7 in. diameter. The circle described by the axis of the wire has a diameter of 1.5 in. This may best be treated as a cylinder bent to a circle. The length of the cylinder is the circumference of the circle plus the overlap. From the tables the circumference of a circle 1.5 in. in diameter is found to be 4.7 in. This plus the overlap of 0.6 gives the length of the cylinder, 5.3 in. The base is the circumference of the wire. From the tables this is found to be 0.7 in. approximately. Then circumference multiplied by length, or  $0.7 \times 5.3 = 3.7$  sq. in., which is the area of the curved surface. The areas of the bases are small and are disregarded. When the specimen has to be treated as formed from a number of geometrical forms, the value of each is computed and the results added. Complex forms such as animal and human figures are handled in the same way, although, naturally, the computation is more complex. The values obtained are entered in the record.

<sup>1</sup>Convenient tables are also found in many Engineers' Handbooks and Pocket-books such as Pender's and Trautwine's.

A few extracts taken at random from the writer's records with brief comments on them will give a general idea of the kind of data needed. These notes are for laboratory use only and have nothing to do with the fuller descriptions in the Museum catalogues. Notes are often supplemented by sketches with dimensions entered on them. Dimensions are indicated by initials, as *L* for length, *D* for diameter, *W* for width, and *Th* for thickness.

1. No. 156738. Pin in three pieces. Light gray surface with green mottling and deep longitudinal cracks. Section near top shows white, chalky core within black ring. Outer third like surface. Top flattened and bent to scroll. No metal in section. Very bad condition. *L*, 5.7 in. *D* at top, 0.3 in. Tapers to point. 2.8 sq. in.

This bronze pin, in spite of its condition, restored perfectly. The white center of the section showed that the removal of the metal and its redeposition as concretion was far advanced but there was a chance that the original surface was inside the leached area. Upon treatment a thin film of copper formed just outside the thin, black ring which was changed to cement copper. The concretionary matter outside the copper film disintegrated into an incoherent slime of cement copper, clay and sand which was readily removed. The restored specimen was fragile until given a hardening treatment. Unfortunately, relatively few specimens have the center exposed and the treatment must usually be given without knowing the condition of the interior. Treatment of bronzes in as bad a condition as this requires considerable experience. This can be gained from treatment of bronzes in better condition.

2. No. V 756-8. Needle. No head, square section. Thin, lumpy crust with much metal showing. Point missing. *L*, 4.3 in. *D* at head, 0.25 in. 2.2 sq. in.

3. No. V 752-1. Tool. Rectangular section slightly curved and tapered to each end. Rough olive coating. *L*, 3.2 in. *D* at center, 0.4 in. *D* at ends, 0.3 in. and 0.2 in. 2 sq. in.

4. No. V 48-2. Hatchet. Rough green coat and gray soil. Good condition. *L*, 4.1 in. *W*, edge, 1.5 in. *W*, head, 1 in.

These are examples of bronzes in good condition readily restored.

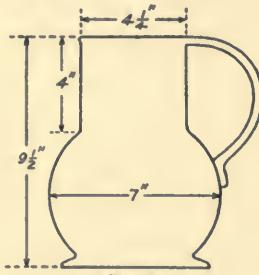
5. No. 31928. Egyptian statuette. Man with tall head-dress. Good condition. Thin, brown patina with dull green patches. Rough in places. No malignant patina visible but looks suspicious. Much detail obscured by rough, dull green patina. *L*, 3.25 in. *W*, 1 in. *Th*, 0.25 in. 15 sq. in.

This is an example of a bronze treated to develop concealed ornamentation.

6. No. 30290. Egyptian lion-headed statuette. Dull green and brown patina. Malignant patina well developed on base. Surface elsewhere firm but rough. Eyes silver. *H*, 9 in. *W*, 2 in. *Th*, 1 in. 40 sq. in.

This is an example of a bronze treated to remove malignant patina which was too strongly developed to be effectively handled by chemical means. The silver eyes were examined and the silver found to be uncorroded, so that it could safely stand the treatment.

7. No. 30148. Egyptian bronze or copper pitcher. Rough grayish-green patina going to brownish in places. Freckles of oxychloride. Metal seems solid. 415 sq. in.



This is an example of a bronze treated to remove corrosive patina and a too thick patina of unattractive aspect. It also illustrates the use of rough sketches to amplify the description.

*Wiring the specimens.*—After the record has been made the specimens are prepared for electrolysis. The first thing to do is to attach a copper wire to each specimen. This wire besides suspending the bronze in the tank conducts electric current to it, so some care is advisable to see that a good electrical connection is obtained. Bare copper wire of 26-gauge<sup>1</sup> is used for most specimens, although heavier wire is used for the larger objects. It is difficult to attach 26-gauge wire to small, fragile objects such as finger rings, and for these the more flexible 30- or 32-gauge wire, hardly thicker than a hair, is used. These wires frequently become hot, but this is of no consequence as the wires are short and bare and the part in contact with the bronze is cooled by the electrolyte. When the crust conducts electricity fairly well, as is the case with most smooth crusts and those showing copper compounds such as malachite or azurite

<sup>1</sup>Brown and Sharpe or American wire gauge.

in more than the smallest quantity, the connection is made by wrapping an end of the wire around the specimen in a close coil of three to six turns. When the surface of the crust is entirely of earthy matter or for other reasons it is suspected that the electrical resistance is high, the wire, after attaching it in the usual way, is carried in a loose spiral over the entire length of the specimen for the purpose of providing a larger contact (Plate III, Fig. 1). When the crust is thick it may happen that the crumbling of the coating during treatment may release the bronze and let it fall to the bottom of the tank. Usually when the crust is thick, the specimen is, at the end of the treatment, resting loosely in the coil of wire, but by that time so much reduced copper has been formed that the electrical connection remains sufficient. Specimens which are mere shapeless concretions and some others in extremely bad condition are wrapped and tied with the wire much as a paper parcel is tied with string. It is sometimes convenient to attach a number of small specimens to the same wire tandem.

Removal of a part of a nonconducting coat in order to provide better electrical contact with the wire at this stage of the treatment should never be attempted. Removal of crust by mechanical means should be undertaken only as a last resort after prolonged attempts at treatment have shown the absolute necessity for it.

After the wire is attached, specimens which the preliminary examination has shown are likely to fall apart along joints, are made secure. They are wrapped with fine wire in such a manner that if they fall apart they will hang in the electrolyte without touching the bottom of the tank. Wire, not thread, must be used, as electric contact must be maintained. When the condition of the specimen makes much wrapping necessary, sufficient wire is used for electrical requirements and the wrapping completed with thread.

Gold inlays can be disregarded. Silver inlays have always been found in good uncorroded condition thus far, except for a thin, velvety, black tarnish. Silver inlays in this condition are disregarded. If a corroded silver inlay were found it would be treated as mineral ornamentation. Other ornamentations thus far found in the Museum laboratory are lapis lazuli, turquoise, agate, onyx, oriental alabaster (Mexican onyx), ivory and bone. Incrustation over these substances is often less than over the rest of the specimen and the ornament may be partially or wholly exposed. When this is the case, the ornament is coated with melted wax or paraffin to protect it from the electrolyte. The electric current does not damage

them. The covering with wax may be an unnecessary precaution, as concealed ornaments of this kind when exposed by the treatment have not been damaged. If an ornament of this kind should be found which was not seriously damaged by age, careful protection with wax would be essential as most of such fresh material is either discolored or eroded by caustic soda.

Sometimes a specimen is found which is very weak. It may be almost a loose powder held together only by an outer skin which the treatment will remove, or it may be of material which experience has demonstrated may disintegrate under treatment. Such a specimen must be treated with extreme care. For such specimens a number of thin, wooden splints are made and wired to the specimen by wrapping with 30-gauge wire. The end of the fine wire is fastened to a heavier wire about a foot long which serves to lead the current in. The specimen is then laid in the center of a square of thin asbestos paper and embedded in coarse, white Ottawa sand or its equivalent so that there is a layer of sand from one-quarter to three-quarters of an inch thick on all sides. The asbestos paper is then folded over, made into a package and tied with thread or string. Two loose ends of string are left for hanging the package in the tank.

*Electrolytic treatment.*—Human and animal figures unless small (less than two inches high), large objects and specimens in exceptionally bad condition are treated separately, that is, each has a separate tank and anode. Three or more tanks are often run at the same time in parallel (Fig. 8). A simple example would be that of a bronze figure, three inches high, treated in a cylindrical glass battery jar. A copper wire about a foot long has already been attached to the figure. A strip of wood one-quarter inch in diameter and long enough to rest across the top of the jar serves to support the figure. The wire is looped once loosely around the wooden strip and secured by twisting once about itself. The wooden strip is laid across the top of an empty jar and the wire adjusted so that the figure hangs in the center of the jar midway between top and bottom. The bronze with its attached strip of wood is then laid aside, while the anode and electrolyte are prepared. For this specimen a sheet iron electrode lining the inside of the tank is suitable. The anode is placed in position and the jar filled with electrolyte. The figure is replaced with care to see that it does not touch the anode. The wire from the anode is then connected to a branch of the positive wire on the rack. The wire from the cathode (the bronze) is attached to a branch of the negative wire (Fig. 8). It is

important that these connections are not reversed. The current is then switched on.

Six or eight small objects may be treated at once in one tank. These may be suspended in a row from a single support and either the wall lining or two iron plates used as anode. In early practice the sheet iron plates were placed one on either side from half an inch to an inch and a half from the cathode. It has since been found that if the plates are spaced as far as possible from the cathode, treatment proceeds more uniformly. At present when rectangular tanks are used the anodes are placed against the sides. It was at first thought that the current would, owing to the unequal resistance of the cathode surfaces, distribute itself so unequally among the specimens that some would take an excess sufficient to damage them.

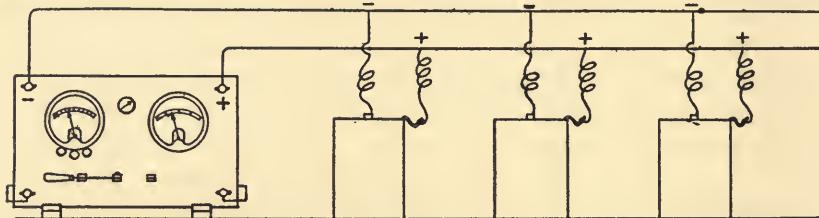


FIG. 8  
Parallel arrangement of electrolytic cells

Such unequal distribution of current must occur, but hundreds of specimens have been treated and none has been damaged. This is probably because the specimens are watched and whenever one evolves gas freely, indicating excessive current, it has been promptly removed for separate treatment.

Hollow objects, such as bowls, vases or jugs, must have specially shaped anodes. The hemispherical anodes for bowls are easily prepared. The diametral length of the curved interior or exterior surface to be treated is measured with a flexible rule or strip of cardboard. A disk of sheet iron is cut to a diameter slightly longer than the measured curve. Starting from points in the circumference an inch apart (less for small anodes), radial cuts are made extending three-quarters of the way or more to the center (Fig. 9). It is now easy to bend these strips by hand to hemispherical form by allowing the adjoining strips to overlap at the edges (Fig. 10). Two anodes are needed for a bowl, one outside and one inside. These are kept from touching the bowl by small pieces of paraffined wood or by pieces of thick asbestos board. The assembly of two anodes and bowl is tied together with string, the necessary wires are attached and the whole suspended in a tank.



COPPER OBJECTS FROM KISH  
Before and after treatment

1 and 2. Rod with one enlarged end, Field No. V-748. Length 5 in. Condition good. Treated for three days at 0.25 ampere. After treatment the enlarged end proved to be an engraved head of a running dog. 3 and 4. Hair-pin with ring. Length 4 in. Condition good. Treated four days at 0.2 ampere.



COPPER HAIR-PINS FROM KISH  
Before and after treatment

1 and 2. Hair-pin, Field No. V-405-M. Length 10.9 in. Condition fair. Treated four days at 0.25 ampere. 3 and 4. Hair-pin, Field No. V-405-L. Length 8.7 in. Treated four days at 0.25 ampere. While 2 and 4 look like solid copper, they really have only a thin copper surface enclosing an oxide core. 5 and 6. Hair-pin with spherical head, Field No. Y-410-L. Length 6 in. Head inset with turquoise and bone(?). Condition very bad. This is an example of a copper which has undergone such extreme alteration that restoration is not possible. Treated for four days at 0.25 ampere.

When the interior of a vase or jug has to be cleaned, a cylinder bent from sheet iron, or a rod, if the opening is small, is used as anode. The anode is suspended so that its end approaches but does not touch the bottom of the hollow. A Bunsen clamp on a lamp stand makes a convenient support. The inside and outside are cleaned simultaneously, the outside being provided with ordinary anodes.

The correct current density is one ampere for each twenty square inches of surface treated. The area of the specimen in square inches divided by twenty gives the current in amperes. As this current density is well below the danger point and as the calculated areas are less than the true, there is ample margin for ordinary variations

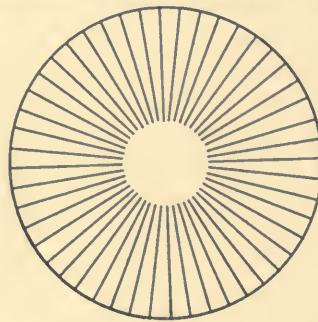


FIG. 9

First stage of manufacture of bowl electrode. Sheet iron with radial cuts

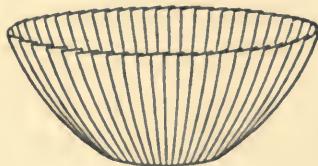


FIG. 10

Finished bowl electrode

of current distribution over the treated surfaces. Extreme variations are detected and cared for later. When the current is switched on, an attempt is made to adjust it by the rheostats to the predetermined value and the readings of the voltmeter and ammeter are noted. With the arrangement of the electrolytic cell described and with specimens having as low a surface resistance as any likely to be treated, the voltmeter will read two and one-half volts when the current density is one ampere per twenty square inches of surface. This voltage, if the current density is kept constant, will be the same whatever the area of surface may be. Increased current required by

## 30 FIELD MUSEUM OF NATURAL HISTORY—TECHNIQUE, No. 3

a larger area is compensated by decreased resistance of the cell with the larger cathode. Usually the voltage will be high at the start and will rapidly decrease with corresponding current increase for the first few minutes of operation for the reasons explained in the next paragraph. A voltage of less than the usual two and one-half may be encountered at times.

The quantity of current passing through the electrolytic cell when a definite voltage is impressed across it depends upon the resistance of the cell. Some decrease of resistance is caused by heating of the electrolyte by the current, more by its thorough mixing, as circulation is induced by evolution of gas from the anode. The important change is a decrease of the resistance of the coating on the specimen. When the coating or a layer of it is of earthy material free from important quantities of metallic salts, it is a nonconductor and current can pass only through the electrolyte which fills its pores. When the bronze is first put in the tank the coating is dry and no current passes. As the electrolyte gradually penetrates the pores, current begins to pass and increases until saturation is complete. Many coatings are a mixture of earthy matters and conducting metal compounds. Such coatings conduct more or less current according to their composition, but pass more current after they are wet. Decrease of resistance follows changes in the composition of the crust due to chemical reduction. A copper mineral, malachite for instance, in the crust, is reduced to metallic copper, which has a small resistance compared with that of the original mineral. No important increase of resistance due to polarization at the anode has been observed.

For these and other reasons the current through the cell often rises rapidly for the first few minutes. When the current is switched on and the meter readings made, one of the following conditions will be apparent.

1. When the ammeter indicates the correct current density the voltmeter may indicate from two and one-half to three and one-half volts. This means that surface resistance at the cathode is low and no important increase of current is to be expected. It is good practice to cut the current to half value for fifteen minutes as a precaution.

2. With the correct current flowing the voltmeter may indicate a higher voltage, usually from four to six and one-half volts. This condition is encountered more frequently than any other. This often corrects itself within three minutes, for which time the meters are watched and the current maintained at its proper value. If the

voltage remains high, the current is reduced one-half for fifteen minutes and, if still high, for an hour. If at the end of an hour it remains high it is assumed that the crust has a permanently high resistance. The current is then restored to full value and the voltmeter reading disregarded.

3. When the highest available voltage is employed, less than the proper current may flow. This is an exaggerated form of condition 2 which is less frequently encountered. It may correct itself in a few minutes but correction often requires from half an hour to an hour. If the condition is present after an hour's running it will be safe to allow as much current as will pass, provided the cell is inspected hourly.

4. Only a minute current or none at all can be forced through the cell by the highest available voltage. This indicates an open circuit for which there may be several reasons. A wire may be disconnected or loosely connected or some terminal may be corroded. The connection between the iron anode and its wire is a frequent source of this trouble. Water may have been used in the cell instead of electrolyte. The trouble is usually due to a nonconducting layer in the coating of the object treated. If the condition is not corrected after an hour's running the treatment should be continued for several days, using the highest voltage available and with hourly inspection. This may be continued for a week if necessary and almost invariably breaks down the insulation. If at the end of a week no current passes, the specimen should be withdrawn and a small portion of the crust removed mechanically to permit better electrical contact between specimen and wire. Removal of the portion of crust may show that the specimen is of alabaster or other untreatable material.

5. Both ammeter and voltmeter register no current. There are several possible causes. It may be that no current is being generated because of some condition in the generator. The generator may be disconnected from the instrument panel. A fuse may have blown. The ordinary cause is a short circuit, either from bare wires touching or from the cathode touching the anode. With some makes of generator instead of no current on short circuit there is a large current. The ammeter needle then runs off the scale on the high side and a fuse blows.

6. The ammeter needle vibrates. This indicates either a partial short circuit, usually from touching electrodes, or a loose connection.

*Conditions during electrolysis.*—The current passing between anode and cathode decomposes the water of the electrolyte. The oxygen of the water is freed at the anode and rises from it in bubbles. The hydrogen is freed against the cathode or specimen. The coating of the cathode is sometimes an essentially pure, firm and strongly adherent crust of oxidized copper compounds. Sometimes it is a concretionary mass of earthy and other foreign matter cemented with oxidized copper compounds which are usually carbonates and oxides. The concretionary mass may extend inward far beyond the original boundaries of the bronze and in many specimens no vestige of the original metal can be found. Other cementing minerals, such as calcite and chalcedony, may be present in smaller quantity. They may, when the copper minerals have been destroyed, cause the coating to remain feebly coherent in places, but such a coating is weak and brittle and its adhesion to the metal beneath has been destroyed. The hydrogen is set free against and within this crust in a very active condition and reduces the copper cementing minerals to metallic copper. Most of the copper takes the form of a dark chocolate-colored slime with no cementing properties. Some of it appears in a redder form very slightly coherent. Usually a little of it takes the form of discontinuous films of metallic lustre. Much of the success of the process is due to the formation of a thin film of bright metallic copper in the position formerly occupied by the original surface of the bronze. The newly formed copper may take the form of a coherent sponge of bright metal.

If the reduction of the copper minerals proceeds rapidly, the specimen may distort or disintegrate. During the first part of the treatment it should not proceed so rapidly that gas bubbles form on the specimen in more than trifling quantities. Bubbles from the supporting wire may be disregarded. It would be better if there were no gassing at the cathode at any stage of the process but in the later stages gassing cannot always be avoided. If the current density is not allowed to exceed its initial value such gassing does no harm. When the electrolysis is proceeding properly with a free evolution of gas at the anode and little or none from the cathode, the coating begins to disintegrate. The electrolyte becomes turbid and a thick scum rises to the surface. Soon a slime of cement copper mixed with earthy matter and fragments of crust collects on the floor of the cell. The greens, blues and reds of the specimen begin to fade and are replaced by a chocolate brown or dark red. The coating usually becomes thinner and may disappear entirely, leaving

a metal surface covered with brown slime. More or less coating usually remains and in many cases there is no perceptible diminution of its quantity. At the close of the treatment such crust as remains is weak and brittle and does not adhere to the surface of the bronze.

The current passing to the cathode breaks down any soluble salts that may be present there into their ions and transports the acid ions to the anode. Most of the bronzes treated have been seriously contaminated with chlorides, chiefly common salt and the basic chloride of copper. These salts are corrosive. They may be in a quiescent state or they may be actively corrosive. Even when quiescent they may become active later and form a malignant patina which will quickly destroy the bronze. Under the influence of the current the chlorides decompose and the chlorine ion on which the destructive action depends is transported to the anode. Other salts such as basic sulphates, which may be injurious, are removed in the same way.

The elimination of chlorides is so important that an investigation of the distribution of chlorine in the cell was made. It is believed that the circulation of chlorides in the cell is substantially as follows: Chlorides in the cathode are decomposed by the current and the chlorine transported to the anode. It is liberated there in an active state. This chlorine combines with the iron of the anode to form ferric chloride. Possibly some may also combine with the caustic soda of the electrolyte to form salt. The ferric chloride goes into solution in the electrolyte and is promptly decomposed, forming salt, sodium chloride, which remains in solution, and basic chloride and hydroxide of iron, which are precipitated and fall to the floor of the cell. Here the basic chloride slowly hydrolyzes and the chlorine re-enters the electrolyte as sodium chloride. As there is circulation of the electrolyte, part of the chlorides in solution return to the cathode, where they are decomposed to pass again through the cycle. It is evident that were it not for the circulation of the electrolyte, nearly all the chlorides would be concentrated in the precipitate and in the vicinity of the anode. Even with a moderate circulation of electrolyte the chlorides are eliminated from the cathode except at the surface, for chlorides brought by the circulation to the cathode are decomposed before they have time to penetrate.

If the chlorides pass through this cycle the following assumptions should be correct. After a cell has been in operation long enough to eliminate the chlorine from the cathode, the chlorine should be more concentrated near the anode than near the cathode. After

### 34 FIELD MUSEUM OF NATURAL HISTORY—TECHNIQUE, No. 3

standing idle for some hours the electrolyte should be richer in chlorine than when the cell is working, as it is being constantly enriched by hydrolysis of the basic chloride in the precipitate. The following chlorine determinations were made to verify these conclusions. Unused electrolyte containing chlorine from impurity in the caustic soda and from the chlorinated city water, contained chlorine to the amount of sixty grams per liter. After the cell had been run on the same specimen for three days so that all chlorine had been removed from the cathode, the electrolyte contained, after standing idle over night, chlorine to the amount of 600 grams per liter. After running thirty-five minutes the electrolyte against the cathode contained 400 grams of chlorine per liter and that against the anode 560 grams per liter. The chlorine content of the electrolyte when idle is materially in excess of the content when it is working, which favors the theory of the hydrolyzation of chlorides from the precipitate. The chlorine content of electrolyte from near the anode of the working cell is 40 per cent in excess of that from near the cathode. The chlorine content of unused electrolyte even when chlorinated city water is used is so small compared with the contamination of the used liquid, that there need be no hesitation in using tap, instead of distilled water. It is good practice to remove the specimens from the cell before shutting off the current, although this probably makes but little difference in the quantity of adhering chlorides. The bare wires may be handled with impunity owing to the low voltage.

*Time of treatment.*—It is impossible to predict from appearances the time required for treatment of any specimen. Some Egyptian bronzes have been finished in three hours and an occasional specimen from Kish has required three weeks. Specimens that seem identical in appearance, size and condition require widely divergent times of treatment. The average time is, perhaps, three days. This means the elapsed time from beginning to end of the treatment. The actual time the specimens are subject to electrolysis is shorter. The treatment continues for only seven hours each day at this Museum, as the generator must be stopped at night. Where it is allowable there is no objection to running continuously night and day. Treatment is finished when the cathode gasses freely even when the current is materially reduced. It has been found advantageous to remove the specimens just before this stage is reached but this point can be determined only by experience. In many cases the end of the treatment can be readily told by the appearance of the surface. When the free gassing of a specimen indicates that it is finished it may

be found that a part only of the surface is finished and that a part of the crust is still firmly adherent. The finished part should then be roughly cleaned and the specimen dried. The exposed metal is then coated with melted wax or paraffin and the specimen returned to the cell. A specimen imbedded in sand and asbestos paper is left until it gasses freely or until the treatment has continued for ten days (seventy hours). When a number of bronzes are treated in one cell they will finish at different times. Each must be removed as it is finished and the proper reduction of current made.

When the specimens are in unusually bad condition, current density is reduced to one-half the prescribed value or one ampere to forty square inches of surface. When the metal to be treated is in the best condition, treatment may be speeded by raising the current density to twice the prescribed value, or one ampere to ten square inches of surface, without injurious results. The condition of the metal must be known with certainty before this is done. Many a seemingly perfect bronze or copper capable of taking a high polish is thoroughly impregnated with oxide, which makes it brittle and readily subject to injury.

When the specimens are removed from the cell they should be washed for a moment in running water and then transferred to the archaeological laboratory to be finished. From time to time a number of pieces may be roughly cleaned in the chemical laboratory so that the chemist may determine the results of the process as the appearance of the treated specimens is sometimes deceptive.

#### CLEANING TREATED SPECIMENS AND PREPARING THEM FOR EXHIBITION

After electrolytic treatment the bronzes are transferred to an anthropological laboratory for finishing. The specimens come to this laboratory with the incrustations loosened from the surface to be exposed and partially removed. The original surface has been restored and the corrosive chlorides eliminated. Here what remains of the incrustation is removed, the bronzes are washed, patinated, hardened, repaired and lacquered. This work requires, for all but bronzes in better condition than the average, the dexterity, skill and experience of an artisan accustomed to repairing and restoring antiques. Forsuch an expert the work presents no especial difficulties, although some of the work will tax his skill to the utmost. The work will proceed along somewhat different lines in different laboratories, according to the experience and judgment of the worker. In Field

## 36 FIELD MUSEUM OF NATURAL HISTORY—TECHNIQUE, No. 3

Museum this part of the treatment is in charge of the modeler of the Anthropological Department, John G. Prasuhn. There are some important features in which this work differs from ordinary restoration, and for these phases of the work Mr. Prasuhn has had the advice of the author. The closest cooperation between the chemical and archaeological workers at all times is necessary if good work is to be done. Although the treatment of all specimens follows the same general lines, differences in the physical condition of the bronzes necessarily make material changes in the details of the treatment.

*Cleaning.*—Sometimes the first stage of treatment completely disintegrates the incrustation, leaving only a slime of dark-brown cement copper, most of which has fallen off. In such cases when the metal is unaltered and has retained its full strength, cleaning is simple. The adhering slime of cement copper can be scrubbed off with brushes. Wire brushes are used when necessary. A few specks of crust will remain, but these are readily scaled off with a wooden or steel point, as adhesion to the metal has been destroyed. After the bronze has been brushed, it may be polished if desired. If, however, a thin film of cement copper is left, an improved patina may be obtained later. The cement copper also fills pits and hence the finished bronze will have a smoother surface than before treatment.

Such unaltered metal is found only in bronzes of relatively recent origin. Specimens more than two thousand years old have been so weakened by an oxidation which extends throughout their substance that they are very brittle. The surface may be so tender that it is easily damaged by cleaning tools and even by the bristles of stiff brushes. The appearance of such bronzes is deceptive. They may, even before treatment, take a brilliant polish and have all the external appearance of sound metal, even when so altered that they have only the consistency of weak chocolate bars. In extreme cases the oxidation has advanced so far that there is little of the original metal left and the bronze assumes the color as well as the texture of chocolate. If this condition is not recognized at once, serious damage may be done before the error is discovered. These bronzes of rotted metal are cleaned in much the same way as are those of sound metal but greater care must be exercised and softer brushes used.

The complete disintegration of incrustation can be effected on only a small portion of the specimens treated. Most of them after electrolysis retain all or a part of the crust in a loose and weakened state which permits its ready removal. What is found under the electrolyzed crust depends upon the condition of the specimen before

electrolysis. The state of the interior of an untreated bronze may often be determined by inspection, particularly when the crust is thin or discontinuous or when the specimen is broken. When the crust is thick, this determination is uncertain and many surprises may be encountered during treatment.

*Corrosion of buried bronze.*—Restoration of the more difficult pieces will be more intelligently conducted if the interior condition of the untreated bronze is understood. What follows refers to bronzes from Kish which were probably buried between 4000 and 3400 B.C. These are in a worse state than the average ancient bronze both on account of their age and because of their high content of salt. No formal research into the corrosion of bronze has been attempted here but such observations as have been made have led to the following conclusions.

When the bronzes were buried, they were already covered with a patina or at least a tarnish of oxides and other compounds of copper and tin. There was also present from handling a thin, greasy coating or impregnation of the patina. The patina or tarnish was chemically stable, continuous over the surface and firmly adherent. The possibility of restoring in metallic form a surface that has entirely gone depends upon the persistence of this film of oxidized metal which differs in composition and physical character from the products of later corrosion. Although the presence of this film has not been proved it is difficult to conceive of any other condition which would allow the restoration in metallic form of a completely lost surface. The substance occupying the position of the lost surface must differ in some way from the surrounding matter. There are other facts which indicate the persistence of this patina. A good patina is dense physically and stable chemically. It is more or less impregnated with oily matter from handling and this affords some protection. This film cannot always be seen, but its presence as a dark-colored circle in the proper position has been noticed on transverse fractures of many pins. The "boils" or irregular lumps of copper minerals which are sometimes found on the accretion surrounding a bronze commonly lie over a pit of the restored surface. This suggests the presence of a surface film which has broken at places and allowed a freer passage of copper-bearing solutions from the interior. Some objections may be urged against the theory. The film is invisible in most cases but the conditions for observation are unfavorable. It might be expected that swelling and distortion of the bronze would disrupt the patina. The restored specimens prove, however, that no

important swelling or distortion occurs. The distortion ordinarily encountered is limited to a slight bending of long, thin objects such as pins and spearheads. The increase of volume by oxidation is more than compensated by the removal of metal in solution. The corroded bronze is more porous than the original.

The process of corrosion is complex and with so many variable elements to consider it is impossible to follow it in detail. Progress of corrosion under the conditions present at Kish may, however, be described in a general way. The patina or tarnish is a protection for the bronze it covers but not a complete protection. It delays but does not prevent corrosion. Water penetrates it through minute fractures and also passes by osmosis. This water often holds in solution air, carbonic acid and various salts which can attack bronze. The corrosion of the bronzes now under consideration is greatly accelerated by the large quantities of salt which the ground waters carry. Nearly ten grams of salt were extracted from a basin thirteen inches in diameter and four inches deep (Plate IX). Some of the products of corrosion dissolve in the water and are removed from the bronze. Others are insoluble and remain where they were formed as a brittle and sometimes incoherent mass of oxide of tin mixed with oxides, carbonates and basic chlorides of copper. Silicates, phosphates, sulphides and basic sulphates have been noticed among the compounds formed and other salts of copper may be present.

Some of the copper removed from the bronze in solution redeposits as oxide, carbonate or in other oxidized form immediately outside the bronze. These newly formed minerals cement loose soil, and any other particles that may lie near, to a firm mass of accretion. When no soil is present the accretion is composed wholly of copper minerals and there is no visible difference between the outside and inside of the mass. The accretion is firmly joined to the film of patina and cannot be separated from it mechanically nor can it be eaten away by acid without destroying the specimen. When the interior of the bronze retains its metallic appearance and there are "boils" on the outer surface of the crust there will be a pit in the metal under the boil which may be so deep that if the specimen is thin and slender it may be separated into two parts.

Cementing materials other than copper compounds may be present in the crust. Those commonly found are calcite, chalcedony and limonite. These minerals, derived from outside sources, are not affected by electrolysis. They are never present in quantity sufficient



COPPER HAIR-PIN FROM KISH WITH FIGURE OF LAMB  
Before and after treatment

1. Before treatment. Field No. X-367. Length of pin proper, 3.3 in. It appeared to be in good condition. It was treated four days at 0.25 ampere. 2. The same after treatment. The head proved to be a male lamb with sprouting horns.



1



2

COPPER BOWL FROM KISH

Before and after treatment

1. Before treatment. Diameter of top 13.3 in. This basin was in bad condition and extremely fragile. Treatment lasted three and one-half days at 15 amperes. 2. The same after treatment and filling cracks.

to provide a firm bond after the copper minerals have been disintegrated, although they serve to hold the crust together as a weak brittle mass easily broken up.

This, the first stage of alteration, frequently proceeds until there is no metal left except in oxidized form. Corrosion may proceed from the surface inward. In this case the metal is first pitted, then becomes thinner and takes the form of a metal core surrounded by a mixture of the mineral products of corrosion. This action may continue until all the metal is gone. The mineral mixture may be without structure or it may be laminated. At the same time a crust may form on the outside but this is sometimes absent. Corrosion proceeds as described from the surface inward in relatively few cases. In the majority the attack seems to be practically simultaneous throughout the mass of the metal. During the first stages of alteration the bronze retains its metallic appearance although much of its substance has been changed to oxide, and it is lighter, more porous and weaker than it was in its original state. In the later stages the content of oxide increases, the bronze loses its metallic aspect and becomes darker in color, until, in its final state, when it has lost all or nearly all its metal, it has changed to a loosely coherent mass of copper oxide of a maroon or dark-brown color. It is then so tender that it must be handled with great care. Alteration of the entire mass and corrosion from the outside may proceed at the same time.

*Rate of corrosion.*—Differences of environment of the buried bronzes, especially with respect to circulation of air and water and the presence of corrosive salts in the surrounding soil, account for the great differences in the state of preservation observed. If the bronze remained absolutely dry there would be no alteration but under natural conditions there is enough moisture to cause some change. If the bronze were permanently under still, pure water, alteration would be slow, as the water would exclude air. Most ground waters, however, have some circulation and carry air and various corrosive salts in solution. When the bronze is repeatedly wetted and dried, the conditions favor its rapid destruction, as the introduction of corroding gases and salts is facilitated.

*Secondary changes.*—Most of the bronzes treated have been subject to corrosion of the above described type only. A smaller number have undergone another change even more serious which makes restoration distinctly more difficult. This is believed, but not positively known, to be a secondary change which begins when the

primary alteration has advanced far. Bronzes which have undergone this change always have a thick crust which is frequently so irregular and distorted that the size and shape of the bronze inside cannot be determined. The specimen may be hollow or there may be a core of sand and clay, sometimes mixed with oxide of tin. There may be deep, longitudinal cracks gaping at the surface and lined with malachite. Sometimes the enclosed bronze is broken and the fragments separated by the injection of matrix into the fractures. Curiously enough these pieces are not, in the bronzes thus far treated, deformed except for occasional slight warping and after treatment the pieces fit together perfectly. When one of these concretionary masses is picked to pieces there is often no indication that there ever was a bronze inside and yet most of them can be restored. All hope of restoration is not gone until the complete leaching away of all metallic salts from the center is so far advanced that it has extended outwardly beyond the original limits of the bronze. The demarcation between leached and unleached zones is usually sharp. The swelling, distortion and cracking of the crust obviously comes from deposition of metallic minerals leached from the interior within the pores of the crust. The mechanism of this transfer is not well understood. Any explanation that can be offered at present is subject to dispute. The transfer of metallic minerals from the interior to the surface seems to be due to a movement of saturating solutions through the pores of the mass as a consequence of alternate wetting and drying. The tentative explanation here given is based on studies of concretion formation in general and of the effects of rising ground waters in arid and semi-arid regions.

The primary cause of this secondary change is the repeated wetting and drying of a bronze which already has a thick crust and in which the primary corrosion is far advanced. During wet periods the interior of the crusted bronze is saturated with water which lies stagnant. This water exerts, owing to its dissolved impurities, a distinctly solvent action upon the cupriferous minerals so that in time the water holds in solution a small quantity of copper salts, a quantity which is greater when such semi-soluble minerals as atacamite and brochantite are present. During a dry period the enveloping soil dries first, the crusted surface next, and the interior last. As the crusted surface dries water is drawn from the interior by capillary action, evaporates from the surface and leaves its dissolved copper compounds there as an addition to the crust. When the newly formed minerals are precipitated, not on the actual surface

but in the pores of the crust, the object is distorted and cracked. Later, surface leaching may remove some of the substance of the crust which is thereby shrunken and further distorted. This shrinkage causes the formation of the deep longitudinal cracks which are sometimes present.

Fortunately relatively few such specimens are encountered. When changes of this kind are far advanced, restoration of the specimens requires much time, care and experience. Unless the operator has the experience and is prepared to give the necessary care and time he may expect to damage many of them.

*Condition after treatment.*—After electrolysis some bronzes will have no coherent crust left and some will have only a thin crust broken into patches which can be lifted off readily. Cleaning these bronzes offers few difficulties and the methods employed have been described. Most of the bronzes retain enough crust to conceal the surface which is to be exposed. The crust is thinner than before treatment and the color has changed. All blue and green is gone except possibly a few green spots left on the tops of "boils." The colors are dull, mostly dark brown, maroon or yellow. Many specimens are ready for cleaning before all the green has faded and, after some experience has been gained, may be recognized and removed from the cell for cleaning before all green has disappeared. They are not injured, however, if they are left until all the green has faded. Some cement copper slime is usually present on the surface and in the pores. The crust is brittle and usually weak so that it may be broken readily by pressure from a steel point or blade. It is usually so coherent that it may be scaled off in small patches but some crusts are so weak that they may be brushed away.

A crust that was originally dense, smooth and deep green, may, after treatment, be strong enough to require considerable pressure from a point to break it, but it is always brittle and free from the surface below. Action in the electrolytic cell is greatest at the surface of the crust and against the original surface of the bronze. Between the crust and the surface to be exposed there will be a thin film of dark-brown cement copper slime or a cellular layer, thin or thick, of bright copper with a honeycomb structure. The cell walls are thin and break down at the slightest touch. This cellular copper can be brushed away nearly as easily as the slime. The electrolyzed crust may be a heterogenous mixture of sand, clay and loosened particles of unchanged crust loosely cemented by calcite or chal-

cedony, or it may have a laminated structure. Occasionally a thin envelope of chalcedony is included in the laminae or very rarely a thin film of bright copper.

The surface to be exposed will present one of several aspects. It may be of bright or tarnished copper. This may be a more or less pitted original surface of the bronze. It may be hard enough to stand ordinary handling during cleaning or it may be so tender that it is easily damaged. When such a metallic surface is hard it is often covered with a thin film of metallic copper which does not adhere well and is inclined to curl off in places. Instead of a metallic appearance the surface may present a brown or red, earthy aspect. Such a surface is composed of minute crystals of cement copper with but little cohesion. The greatest delicacy of handling during cleaning is imperative and sometimes special methods must be employed. When a metallic surface is encountered it, in many instances, is not the original unchanged metal, but a thin film of new copper reduced from the patina which covered the original bronze. Why this thin film of oxide should reduce to a specular continuous film when most of the reduced metal assumes the form of cement copper slime, is something of a puzzle. Deposition in specular form is favored by the dense continuous structure of the patina and possibly by the presence of organic colloids, as these are frequently employed for this purpose in electrolytic copper analyses. The film of copper may be so thin that it is easily damaged by cleaning tools, especially if the underlying surface is soft, or it may be thick and capable of standing considerable abuse. Below the copper may be an original, more or less pitted metal surface, a layer of oxidized matter surrounding a metal core or only mineral products of corrosion.

Cleaning is effected with little difficulty when the crust is nearly or entirely disintegrated. When, as is usually the case, the electrolysis leaves a more or less coherent crust covering much or all of the surface, cleaning is more difficult. In such a case cleaning is started cautiously and the methods employed will differ according to the judgment and experience of the operator.

In the Museum a process of chipping has been found adapted to most specimens. A small piece of crust is cautiously removed by a steel point or blade and the character of crust and interior surface noted. Most specimens are more fragile than they seem and no unnecessary strain is put upon them during this stage of restoration. The crust is always brittle. When it is firm it can be flaked away by pressure of a point or blade, often in fragments of considerable size.

Often there will be some patches which will not readily separate from the surface below. These should not be forced off. The bronze should be allowed to dry to permit most of the remaining crust to loosen from warping and shrinkage. When some of the crust remains adherent after drying, it will often loosen at the edges. These edges then may be scaled away, leaving new edges which in turn loosen in a few minutes and then may be scaled. If some patches remain adherent, the electrolytic treatment has been insufficient and the bronze should be returned to that stage of restoration. Certain kinds of crust remain hard even when adhesion to the underlying bronze has been completely destroyed. Such a crust is as brittle as glass and once a start has been made it is readily chipped, although strong pressure by the chipping point may be necessary.

After the hard crust has been separated the bronze may need brushing to remove slimy matter and small particles. If a metallic surface is exposed it may be polished or left dull as desired. It is the present practice in Field Museum to leave, whenever possible, a thin film of cement copper to improve the patina acquired in a later stage. If the restored surface is pitted, an attempt, not always successful, is made to retain in place the cement copper which fills the pits. When it can be retained the copper filling at a later stage amalgamates with the pit walls so firmly that when restoration is complete the former existence of pits cannot be discerned. It is often not possible to keep this filling in place and refills are not as effective.

*Cleaning by acid.*—Acid cleaning is never tried except as a last resort in the few cases where no other method will serve, and these are few. The method is uncertain and likely to injure the bronze.

Sometimes a brown cement copper surface may be so friable that the last of the coating cannot be safely removed mechanically. This is especially the case where there is incised ornamentation. The cleaning is carried as far as possible by mechanical means before the acid is resorted to. The acid used is a mixture of one part of nitric acid with four parts of water. Under no circumstances should hydrochloric acid be used. The specimen should be hung by a thread in a tank of acid and be inspected at frequent intervals. Action is vigorous. Cleaning is due to a selective action of the acid. It dissolves the fine crystals of copper in the crust faster than it does the larger crystals of the surface to be cleaned. When the cleaning

is complete, action can be stopped by dipping the bronze in water. This treatment must always be carried on where there is good ventilation, for the fumes evolved are injurious to health.

*Washing.*—The cleaned specimens must be washed thoroughly. Most of them are porous. The caustic soda from the electrolyte is persistently retained in the pores and can be removed only by prolonged washing. If it is not removed a carbonate of soda is formed which effloresces as a white bloom. The efflorescence may continue to form for years and during its formation it may damage the new surface. The early practice at Field Museum was to wash the specimen for a time in cold, running water and to follow this by boiling water. The present practice is to omit the boiling water and greatly prolong the washing in cold, running water. It is good practice to leave the bronzes in the running water for at least twenty hours and even longer when the bronze is large or has an unusually porous center.

*Repatinating.*—After washing, the bronzes are repatinated by allowing the finely divided cement copper crystals to oxidize spontaneously. Much of the reduced copper is in the form of loose crystals, so small that they are almost pyrophoric. At the first drying of the bronze these crystals oxidize so rapidly that the specimen often becomes too hot to hold in the hand. Most specimens are dried at some time during the removal of the crust, so that this first oxidation is usually completed before the bronzes are washed. The oxidation begins suddenly at a certain stage of drying, proceeds with vigor and is completed in a few minutes. It causes a cementation of loose crystals and strengthens the specimens. Any thin film of cement copper left on the surface may become firmly attached to the surface, but this is true only for very thin films. This first oxidation forms a patina which is sometimes sufficient but often is little better than tarnish. After the washing the patina must be strengthened. The practice in this regard is not yet standardized and modifications are to be expected in the immediate future. Reinforcement of the patina is secured by providing conditions which favor the slow oxidation of those particles of cement copper which are somewhat larger than those which suffer the first quick oxidation. The conditions can be simply provided by placing the wet bronzes as they are taken from the washing tank near a window where they will be in direct sunlight. They can be left there for several days if necessary. They soon acquire a dark-brown

coating of good thickness, texture and color. This is a true patina, which is derived from the substance of the bronze by the same natural processes as those which produced the original patina. The state of the bronze after treatment is such that the patina forms in hours instead of years, and without the use of chemical washes or gases. The process is erratic and results cannot be predicted. About 20 per cent of the bronzes will not patinate and there seem to be some factors present which are as yet unknown.

*Impregnation.*—Many bronzes are at this stage decidedly fragile. These can be hardened by impregnating with celluloid. There is a great diversity in the properties of the many celluloid cements and lacquers on the market. The celluloid solution for this use must be thin and transparent, also it must be colorless and invisible when applied as lacquer. Most important of all, it must penetrate well. The celluloid solution used in Field Museum laboratory is the lacquer called "zapon," much used by silversmiths. Bronzes to be hardened are, if small enough, soaked in zapon. It is applied to larger bronzes with a brush. Although good results are obtained in this way, better effects could be secured where a good vacuum pump is available by a system analogous to the vacuum system used for treating railroad ties to prevent rot.

*Repairing.*—Broken parts are cemented, using zapon for cement. Any restoration desired can be made at this time. No cements containing chlorides should be used for these restorations as they may make serious trouble later.

*Lacquering.*—The bronzes are now inspected for imperfections which are remedied if possible. It will be found that fine lines of engraving have partly filled and must be cleared. When satisfied that all that is necessary has been done the work is finished by giving the surface a thin coat of zapon lacquer.

This is a description of the average treatment given average specimens. Many deviations will be made necessary by the many variations in the condition of the materials treated and these deviations must depend on the judgment of the operator.

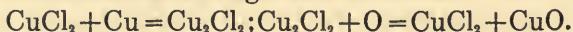
#### MALIGNANT PATINA

A good patina on bronze is something much to be desired. The best patinas are the products of the slow corrosion of the surface of the bronze by atmospheric agencies. This corrosion is so slow that years pass before it attains perfection. It is probable that the best patinas owe much of their beauty to a slight impregnation by oily

substances coming from handling and polishing. These oils or greases fill the pores and, though minute in quantity, affect the luster and to a lesser degree the color. Such a patina protects the bronze and the attractive color, texture and luster add much to its beauty.

There is another kind of patina, corrosive in its nature and unattractive in appearance, which not only is undesirable but must be eliminated whenever it is present. This, the malignant patina or bronze disease, will in time utterly destroy any bronze infected with it. It is due to the presence of a copper salt which has the property of abstracting oxygen from the air and transferring it to the solid bronze without destroying itself during the process. It has no relation to ordinary decay. The tin disease which attacks pewter is of an entirely different character. There are a number of copper compounds which might conceivably act in this manner but the only one found in Field Museum has been chloride of copper. As this compound constantly renews itself, the most minute quantity is theoretically capable of destroying the largest bronze. The smallest speck of it must be eliminated if the prospect of serious damage is to be avoided. There are three principal ways by which bronzes become infected with this chloride. If they remain long buried in salty soil, the salt attacks the copper and forms the objectionable compound. It may come from cleaning with hydrochloric acid. Serious infection also occurs when a plastic containing chlorides is used for restoration.

The continuous action which permits a little chloride to destroy a large bronze is a consequence of the readiness with which copper combined with chlorine changes its state of oxidation and the ease with which it forms basic salts. There is a cyclic succession of changes, the chloride alternately attacking the bronze and renewing its activity. Cupric chloride in contact with bronze abstracts copper from the alloy and is reduced to cuprous chloride which is not corrosive. Cuprous chloride in contact with water and air (the small quantity of air dissolved in many ground waters is sufficient) is oxidized to a basic cupric chloride. As the chlorine of the basic salt is sufficient to bind firmly only half of its copper, the excess copper soon separates as oxide, leaving the regenerated cupric chloride to repeat its attack on the bronze. The details of these reactions are complex and involve the formation and decomposition of basic salts in a way that has not been fully worked out. The general nature of the corrosion can be indicated by simple formulae if only the initial and final stages are considered.





1



2

SEALS FROM KISH AFTER TREATMENT

1. Fallow deer engraved on seal of ring. Field Mark, Acc. 1497-H. Enlarged. Diameter of seal 0.7 in. 2. Impression from seal of a copper ring. Enlarged. The figure of a lion and his kill is indistinct as the seal is badly pitted. Diameter of seal 0.7 in.

FIELD MUSEUM OF NATURAL HISTORY

TECHNIQUE, NO. 3, PL. XI



BRONZE EGYPTIAN PITCHER

Museum No. 30162. Lower part treated, upper part untreated

The basic chloride intermediate stages are always present in abundance in malignant patina and the recognition of these light-green, powdery substances is the usual method of determining its presence. Harmless mixtures of green carbonate of copper with oxide of tin, kaolin and other white powders often imitate a malignant patina. When the copper has been removed from bronze, tin is left in so finely divided a state that it changes to its white oxide at once. Secondary changes soon convert much of the oxide of copper to carbonate and less often to silicate, basic sulphate, phosphate and other compounds. These changes cannot occur in the complete absence of water, but so little moisture is necessary that reasonably dry museum air contains enough to allow rapid corrosion.

Malignant patina is erratic in its action. It may remain inert for years and then suddenly become active for no known reason.

As damage by malignant patina depends upon three factors—presence of air, moisture and more or less mobile chlorides—the effective control of any one of them would prevent all damage. Unfortunately most methods of control are impractical. Some of those which have been used are as follows.

1. Leaching. As many of the chlorides present are readily and the others slightly soluble in water, it might be thought that prolonged leaching may be effective. The solubility of some of the chlorides is so slight that the time of leaching would have to be prolonged far beyond any practicable limits. Nevertheless, prolonged leaching in running water of bronzes sound enough to endure the treatment should delay the destructive action of the patina in many cases, although it cannot stop it. Bronzes should be dried immediately after this treatment by several washes in alcohol or corrosion will be accelerated instead of retarded. This treatment will often be ineffective and at best is merely a palliative. It is never employed in Field Museum. The addition to the leaching water of substances such as ammonia in which the chlorides are readily soluble is barred because the oxides and other copper salts present in quantity in many antique bronzes are dissolved by them and the bronze falls to pieces.

2. Exclusion of moisture. Complete exclusion of moisture both from the bronze and the surrounding air would prevent all damage but this exclusion must be so complete that it can be attained only under laboratory conditions or by special methods of exhibition. The drier the air the slower is the corrosion.

3. Exclusion of air. Complete exclusion of air prevents all damage. The belief that a good coat of lacquer prevents access of air to the bronze surface is erroneous. No lacquer that is absolutely impervious to air is known. Enough air can penetrate the best lacquer through imperfections and by osmosis to permit continuation of corrosion. Corrosion under a lacquer is often more injurious than corrosion of an unprotected surface. Even impregnation with waxes or lacquers is ineffective.

The following method of exclusion of moisture and air is successfully employed by the Department of Geology of Field Museum to check a corresponding disintegration of iron meteorites when they are impregnated by the chloride of iron, lawrencite. These irons are displayed in museum jars in which they are completely submerged under the colorless, medicinal mineral oil known as stanolax. The nature of the oil is important and the one used was selected only after much experimentation. This treatment has not been applied to bronze but it should be effective. The method of exhibition in jars, however, is awkward and in some cases the oil may acquire an objectionable green color. If this treatment is used the bronze should be dried first for several hours at from 105° C. to 120° C. and cooled in a desiccator. This treatment of bronze should be regarded at present as experimental.

4. Surgical treatment. When the malignant patina is confined to a few surface patches it may be bodily excised by the use of scrapers, files and drills. If the excision is so complete that no particle of oxidized matter is left on the brightened bronze surface the treatment will succeed. This is the best treatment for some specimens, although these are relatively few. It often involves serious disfigurement of the surface and where some patches of malignant patina are visible there is often much more dormant.

5. Electrolysis. The Fink electrolytic process for bronze restoration also eliminates malignant patina and is the only known method effective when, as is frequently the case, the malignant salts impregnate the mass of the bronze. It is much used in this Museum to eliminate malignant patina which is present on the surface only and is the only method employed here when it is expected that the malignancy extends below the surface. Three possible modifications of the process may be employed to increase its efficiency when the destruction of malignant patina is the only purpose of the treatment. None of them have yet been tried here as the usual procedure has been found sufficient. These modifications are: (a) The electrolyte

may be changed frequently. (b) A diaphragm or porous cell may be used to prevent recirculation of contaminated electrolyte to the cathode. (c) Silver-plated anodes may be used and the chloride ion precipitated at once from the system. When malignant patina is removed by this process from a specimen which retains a good patina over part of its surface the good patina will be destroyed or seriously injured. This injury can be avoided by heavily coating the good patina with wax or paraffin. This should not be done unless it is known that the malignant material is confined to the surface or to parts of the bronze immediately under the visible malignant patches. It may be necessary to sacrifice the good patina to save the specimen.

6. Chemical treatment. When the malignant matter is confined strictly to the surface it may be rendered inert by a simple chemical treatment recently devised in the chemical laboratory of Field Museum. This treatment first precipitates the chloride in an inert, insoluble form and then renders harmless any possible injurious by-products of the precipitation. The surface to be treated must be dry. A dilute solution of sulphate of silver is applied to the affected surface with a camel's hair brush. This precipitates the chlorides from the malignant patina as silver chloride. The solution is allowed to remain for two minutes. The excess is removed by blotting paper. Then a saturated solution of barium hydrate, turbid with undissolved hydrate, is applied in the same way. This is left for at least five minutes and the bronze is then thoroughly washed. The barium hydrate destroys the excess of silver sulphate and converts the possibly harmful sulphate of copper formed during the first precipitation to a harmless hydrate. Part of the barium hydrate is converted to the harmless sulphate and any excess not removed by washing soon changes to an inert carbonate. The silver solution is used dilute and its time of contact with the bronze limited because it attacks bronze, but its corroding action is temporary. This process is still in the development stage at Field Museum. Studies are now under way to determine the speed with which cuprous chloride is destroyed and to investigate a possible improvement involving the use of ammonia. It is probable that, owing to its slight solubility, the cuprous chloride is not wholly destroyed in the two minutes allowed but that the reaction is completed by the continued action of silver sulphate occluded in the pores of the chloride. Reports have been received of the successful use of the process by dipping the bronzes instead of using a brush. The most suitable

50 FIELD MUSEUM OF NATURAL HISTORY—TECHNIQUE, No. 3

strength of the silver sulphate solution has not been determined. All highly dilute solutions seem to work equally well. This solution may be prepared in advance as, when protected from light, it keeps well. The strength of the barium hydrate solution is immaterial. The present practice is to use a saturated solution turbid with excess hydrate. The solution, which must be in distilled water, does not keep and should always be freshly prepared. The powder from which the solution is made must be kept tightly corked at all times. When some of the powder is removed for use the bottle should remain uncorked for the shortest possible time.

This process is adapted only to bronzes with malignant matter confined to the surface. The process is new and although some bronzes were treated more than a year ago, at least ten years must pass before it is definitely known that the cure is as permanent as it is believed to be.

Three of the methods discussed may be recommended: (1) A small area of malignant patina may sometimes be cut away without materially mutilating the bronze. (2) The electrolytic treatment is sure, is universally applicable and is the only known successful treatment for many cases. (3) When the malignant salts are confined to the surface the chemical treatment with silver sulphate is recommended. Treatments depending upon lacquering or impregnating may retard corrosion for a time but will eventually fail.

The methods discussed in this paper are the only ones as yet investigated at Field Museum.

## INDEX

Agate 26  
Alabaster 26  
Anodes 18, 28  
Apparatus used at Field Museum 12  
Artificial patina 11

Bone 20, 26  
Bronze disease, see malignant patina  
Bronzes in poor condition 35, 36  
Bronzes not treatable 20

Cement of incrustations 38  
Chlorides 11, 33, 46  
Cleaning by acid 12, 43  
Cleaning after treatment 36, 43  
Condition after electrolysis 41  
Condition before electrolysis 9, 32  
Conditions during electrolysis 32  
Corrosion of buried bronze 37  
Corrosion, rate of 39  
Corrosion, secondary 39  
Current control 15  
Current density 29, 35  
Current supply 14

Deformation 10, 32  
Distribution of chlorine in electrolyte 33

Egyptian bronze 11, 12, 21  
Electrolytic cells 16  
Electrolytic treatment 19, 27  
Electrolysis, conditions during 32  
Electrolysis, end of 35  
Electrolyte 17  
Examples of treatment 24

Fink process 7  
Fractures 11, 21  
Fragile bronzes 27

Gold 19, 26

Hollow objects 28

Impregnation 45

Interpretation of instrument readings 30  
Iron 20  
Ivory 20, 26

Lacquering 45  
Lapis lazuli 20, 26

Malignant patina 11, 22, 33, 45  
Malignant patina treatment  
    Chemical methods 49  
    Electrolysis 48  
    Exclusion of air 48  
    Exclusion of moisture 47  
    Leaching 47  
    Surgical methods 48  
Measuring instruments 15  
Meteorites 48  
Mineral ornaments 20  
Motor generator 14

Onyx 20, 26

Patina 9, 37, 45  
Patina, malignant, see malignant patina  
Protection of surfaces not to be treated  
    26, 35

Records 22  
Records, examples of 24  
Repairing 45  
Repatinating 44  
Resistance of incrustations 30  
Restored and repaired bronzes, effect  
    on 11, 21

Silver 19, 26  
Surface area computation 22

Time of treatment 34  
Turquois 20, 26

Washing 44  
Wiring 25

